

Chemical Experiments



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Current status and future of transactinide heavy element chemistry

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1. Introduction

The knowledge and understanding of the chemistry of the superheavy elements, especially of the early transactinides Rf, Db and Sg and their compounds, both experimentally and theoretically, is nowadays quite extensive as documented by a first textbook entitled "The Chemistry of Superheavy Elements" edited by M. Schädel [1]. While rapid chemical separations in aqueous solution were (and are) the method of choice for detailed investigations of Rf and Db, the development of gas-phase chemical separation methods have allowed first chemical studies of increasingly heavier transactinide elements.

The spectacular results obtained at Flerov Laboratory in Dubna using ^{48}Ca ion beams and targets of ^{238}U , $^{242,244}\text{Pu}$, ^{248}Cm and ^{249}Cf to synthesize isotopes of elements 112 [2], 114 [3,4], 116 [5] and 118 [6] give chemists the perspective to experimentally investigate the chemistry of even the heaviest known elements. Especially since some of the isotopes attributed to elements 108, 110, 112, and 114 seem to have half-lives of the order of seconds to minutes.

2. Status

Since 1999 when the first TAN conference was held in Seeheim, Germany, chemists have made a quantum leap and are now working with nuclides that can be produced with picobarn (10^{-36} cm^2) cross sections only. One of the highlights of TAN'99 was the announcement of the first gas-phase chemical isolation of bohrium ($Z=107$) as volatile BhO_3Cl using the OLGA technique [7]. The nuclides ^{266}Bh and ^{267}Bh were produced in the reaction $^{249}\text{Bk}(^{22}\text{Ne}, 4,5n)$ with maximum cross sections of about 100 pb [8]. Even though the experiment was successful and deserved highest scientific merits, the outlook to apply the same technique to the investigation of even heavier elements was bleak, since the overall efficiency to detect a correlated mother-daughter α -particle decay chain was only about 4%. The experimental chemical investigation and characterization of the next heavier transactinide element hassium has, for some years, constituted a daunting task even though from the very beginning the selection of a volatile compound was absolutely clear. Hassium, as a presumed member of group 8 of the Periodic Table and thus a homologue of Fe, Ru, and Os, should form stable and at the same time very volatile HsO_4 molecules, very similar to OsO_4 . However, in order to gain access to hassium ($Z=108$) the overall efficiency of the experiment had to be improved by at least one order of magnitude. By developing a completely new approach of separation (IVO) [9] and detection (CTS, COLD) [10] and also by introducing the rotating target set-up ARTESIA [11], which allowed the use of much higher beam intensities, the first chemical characterization of Hs became reality [12]. This spectacular progress however is limited to a few selected cases which chemically are extremely favorable. One such case is also element 112 in its elemental state. First experiments made in Dubna [13,14] and recently at GSI [15] seem to indicate a quite spectacular difference in chemical behavior between element 112 and its lighter homolog Hg in the elemental state. Compared to chemical investigations of the early transactinide elements Rf through Hs, where always the highest possible oxidation state was investigated, now with elements 112 through 118,

which are expected to be moderately to highly volatile in the elemental state, the influence of relativistic effects of the valence electrons should become noticeable in direct experimental investigations. These relativistic effects might be responsible for some quite dramatic differences in chemical behavior as this seems to be the case in the adsorption properties of element 112 compared to its lighter homologue Hg [16].

Experiments on the aqueous chemistry of transactinide elements focused mainly on a much deeper understanding of the properties of Rf in solution [17]. A fully Automated Ion exchange apparatus coupled to a Detection system for Alpha-particle spectroscopy (AIDA) developed at JAERI, was used to extensively study the behavior of Rf in pure HCl solution [18]. Future experiments with Db using the reaction $^{248}\text{Cm}(^{19}\text{F}, 5\text{n})^{262}\text{Db}$ are planned [18]. A series of trendsetting experiments were performed by the SISAK collaboration [19]. The nuclide ^{257}Rf was produced in the reaction $^{208}\text{Pb}(^{50}\text{Ti}, 1\text{n})^{257}\text{Rf}$, separated in the Berkeley Gas-filled Separator (BGS) and transferred to a gas jet using the Recoil Transfer Chamber (RTC) [20]. The activity delivered by the gas jet was dissolved in nitric acid and Rf was extracted into dibutyl-phosphoric acid in toluene. The decay of Rf nuclides was registered on-line by flow-through liquid scintillation counters. This was the first time a transactinide element was extracted and unequivocally identified by the SISAK system. The use of the BGS provided the necessary reduction of background from interfering by-products of the nuclear reaction. Another approach to extend liquid-phase chemical studies to heavier transactinides is the so-called Multi Column Technique (MCT) [21]. In this continuous on-line chromatography, the solution containing the dissolved transactinide element passes through a series of columns. The transactinide element of interest passes a first column where only its actinide daughter nuclei (and other actinides) are retained. The transactinide element is then retained on a second column. However, its actinide decay daughters pass this column and are retained on a third column from which they are eluted after completion of the experiment and assayed by alpha-particle spectroscopy. This technique is very efficient and allows to access relatively short-lived nuclei. However, a breakthrough even of a small fraction of actinides in the first column can ruin the experiment. Also, all information about the nuclear decay properties of the transactinide element is lost.

Heavy element chemistry is not only dependent on outstanding radiochemists, but also on the necessary infrastructure consisting of powerful heavy ion accelerators and facilities and equipment to produce and handle highly radioactive and also extremely valuable exotic target materials such as ^{248}Cm . In this respect the greatly reduced availability or even the closure of the 88-Inch cyclotron at LBNL without adequate replacement signifies a hard blow to our community. In this respect it is of importance to note that new groups have entered the field of transactinide chemistry, such as the group at JAERI. Remarkable is also the synthesis of the new nuclide ^{259}Db at IMP Lanzhou, China [22] allowing also future transactinide chemistry experiments.

3. Future of transactinide chemistry

The spectacular results obtained at Flerov Laboratory in Dubna in the synthesis of new superheavy elements already have stimulated chemists to experimentally investigate the chemistry of even the heaviest known elements. A first step into this direction certainly are the chemical experiments performed with the spontaneously fissioning nuclide $^{283}112$. Nevertheless, it is highly desirable to develop techniques that are sensitive to reveal also isotopes that decay by chains of α -particles in order to independently verify the results obtained by kinematical separator systems.

What are the prerequisites to achieve the ultimate goal of chemically identifying a new, superheavy element? Due to the very low production cross sections of 1 pb or less highest possible beam intensities must become available in the near future. This ultimately calls for a new accelerator capable of delivering a continuous beam of up to $5 \cdot 10^{13}$ ions/s. Evidently, this also calls for improved target irradiation facilities,

since target thicknesses of the order of 1 to 1.5 mg/cm² are useful. Nevertheless, the experiences with ARTESIA clearly demonstrated, that this setup already today allows accepting a 3 to 4 fold higher beam intensity if a DC beam were available instead of a pulsed beam.

Chemical separation procedures need to be improved with respect to sensitivity and speed. Here, gas phase chemical separations will play an important role, since many of the superheavy elements with atomic numbers between 112- 118 may be moderately or even highly volatile in their elemental state. Thus future experiments point to investigations of elements 112 and 114 in their elemental state. However, a particularly difficult problem constitute some Rn isotopes, since their Po daughter nuclides decay with α -decay energies which strongly interfere with the detection of heavy transactinide nuclides. Especially element 112 seems to exhibit a very similar volatility as Rn. A possible solution to this problem, although not yet available, may constitute a dedicated kinematical pre-separator which is coupled to chemical set-ups. A workshop held at GSI in 2002 clearly demonstrated the future need for such an instrument. Possible pathways to gas chemical investigations of element 112 and 114 are outlined in Fig.1. The currently most convenient production reaction of element 114 is the reaction $^{48}\text{Ca}+^{244}\text{Pu}$.

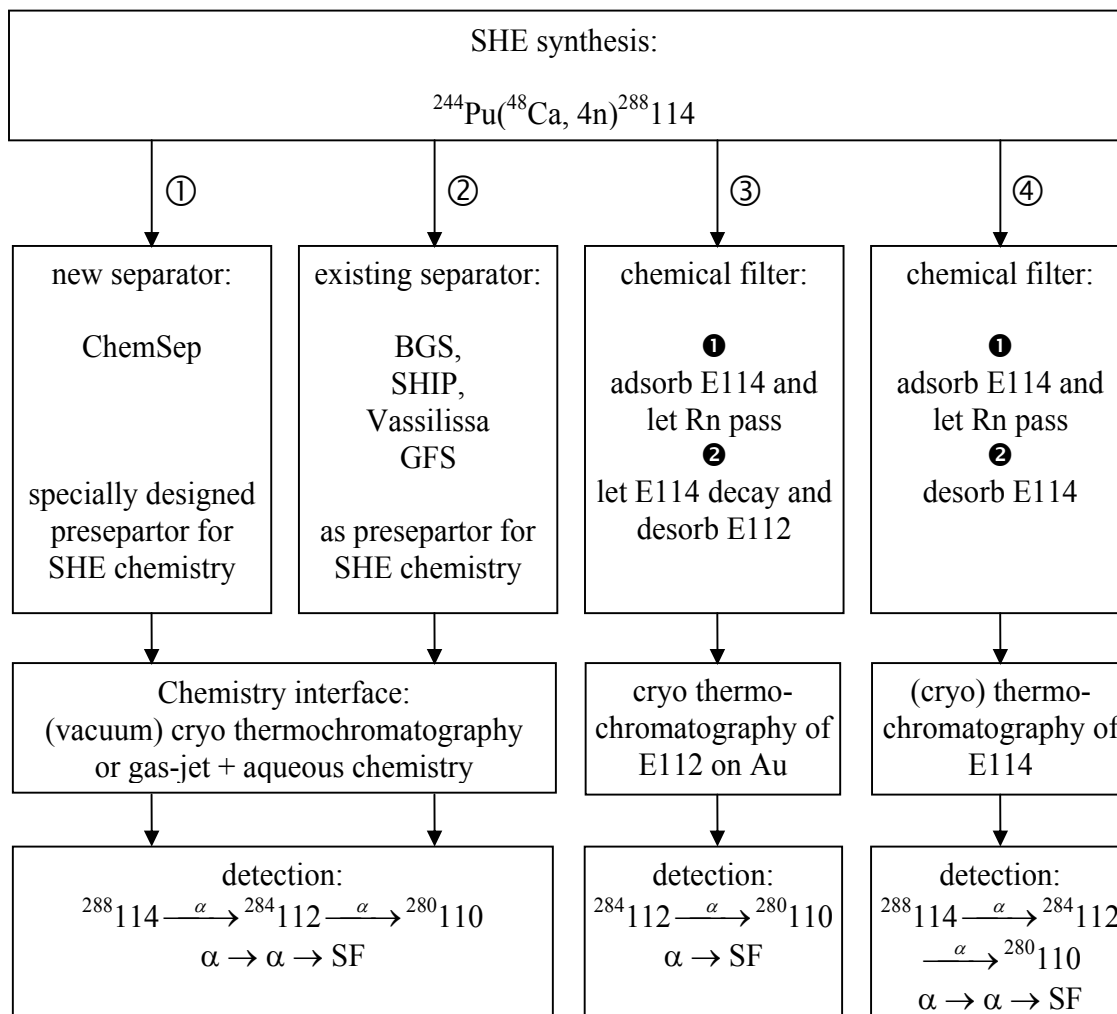


Figure 1. Routes to chemical investigations of SHE providing the unambiguous identification of the investigated nuclides.

Even more challenging than the investigation of elements 112 and 114 is probably the chemical identification of elements 109 through 111, the heavy analogs of Ir, Pt, and Au. Here, no obvious chemical properties or compounds as for instance with group 8 elements are at hand. Again, the use of a kinematic preseparator of nuclear reaction products might considerably facilitate chemical investigations.

The fact that some isotopes of elements 112 and 114 have half-lives of the order of seconds to minutes indicates that there exist similarly long-lived isotopes of elements 113 and 111 that are accessible with current projectile and target combinations. Also here, no chemical separation schemes have been worked out, which would allow an immediate experimental investigation.

To conclude it is fair to say that chemists have made enormous progress in investigating the chemical properties of transactinide elements and certainly the successful hassium experiment will serve as a textbook example for years to come. With the synthesis of relatively long-lived superheavy elements with $Z=112-118$ chemists are facing an extremely challenging but also rewarding future. The possibility to experimentally characterize the complete 7th row of the periodic table has never become more real than starting with today.

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Gas phase chemistry of bohrium (element 107)

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The transactinide element bohrium (Bh, element 107) was discovered in 1981 at GSI Darmstadt, Germany [1]. The systematic order of elements in the periodic table suggests Bh to be a member of group 7, together with manganese, technetium, and rhenium. Doubts about an unchanged periodicity of chemical properties along the rows of the periodic table rise especially for the heaviest elements. The fields of their highly charged nuclei may lead to strong relativistic effects deviating the order in the electron shell structure [2-4]. Relativistic effects force a stronger attraction of the relativistic electron orbitals with a spherical shape (s and $p_{1/2}$) to the nucleus. The resulting shielding of the nuclear charge causes an expansion of the other p-, d-, and f- electron orbitals - the indirect relativistic effect. Therefore, chemical properties as for example ionization potentials, binding energies and geometries of the electron orbitals of the heaviest elements and their compounds may be strongly influenced by relativistic effects. The chemical studies of rutherfordium (Rf, element 104), dubnium (Db, element 105) and seaborgium (Sg, element 106) revealed a typical behavior for members of the transition metal series in the groups 4 to 6 of the periodic table, respectively [5].

Prior to the studies described in the current presentation, two attempts to search for long-lived isotopes of bohrium and to study chemical properties of this element have been conducted in 1984 at JINR in Dubna, Russia in the reaction $^{249}\text{Bk}(^{22}\text{Ne}, 4-5n)^{266,267}\text{Bh}$ [6] and in 1992 at LBNL Berkeley, USA in the reaction $^{254}\text{Es}(^{16}\text{O}, 4-5n)^{265,266}\text{Bh}$ [7]. In both experiments Bh was assumed to form a volatile oxide or oxyhydroxide similar to its homologues in group 7 of the periodic table, Tc and Re. Gas phase chemical separations have been carried out. The cross section limits reached in these experiments were about 0.1 nb in Dubna and about 1 nb in the experiment in Berkeley. Both experiments were not sensitive enough to measure the decay of the Bh-isotopes $^{265-267}\text{Bh}$. Meanwhile, neutron-rich isotopes $^{266,267}\text{Bh}$ have been discovered at the LBNL Berkeley [8] in the heavy ion induced nuclear fusion reaction $^{249}\text{Bk}(^{22}\text{Ne}, 4-5n)$ revealing the enhanced nuclear shell stabilization against spontaneous fission (SF-) and α -decay, which is predicted and experimentally confirmed for deformed nuclei close to ^{270}Hs (Hassium, element 108) [9-13]. The half-life ($T_{1/2}$) of about 17 s and the predominant α -decay mode ($E_{\alpha} = 8.83 \pm 0.03$ MeV) made ^{267}Bh an ideal nuclide for fast gas chemical experiments. The production cross section of ^{267}Bh at a ^{22}Ne energy of 117 ± 1 MeV was about 60 pb, indicating the necessity of an exceptional sensitive experimental chemical approach. Hence, gas phase chemical model studies with Tc and Re were conducted in preparation of the experimental chemical characterization of the transactinide element [14, 15]. The gas phase separation of the volatile oxychloride species of these elements, presumably MO_3Cl (M=Tc, Re) in a low temperature isothermal gas chromatography, based on the OLGA technique [16], appeared to be most promising in terms of separation yield, quality, and velocity. The results of these model experiments were used for empirical predictions of the behavior of Bh in the reactive gas system HCl/O₂. The most stable gas phase compounds and their behavior in a gas-solid adsorption separation have been predicted. From thermochemical extrapolations the standard adsorption enthalpy of BhO_3Cl on a fused silica surface, $\Delta H_{\text{ads}} = -75 \pm 12$ kJ/mol, was predicted [17]. With a physisorption model adjusted to the experimental results with Tc and Re Pershina and Bastug [18] estimated $\Delta H_{\text{ads}} = -78 \pm 5$ kJ/mol.

The Bk-target preparation was conducted at LBNL. A HDEHP redox-extraction separation procedure for Pb, Bk, and Cf was carried out using ultra pure chemicals and carefully cleaned tools in an exceptionally clean glove box endeavouring to avoid accidental heavy metal contaminations.

Subsequently, a target of ^{249}Bk ($670 \mu\text{g}/\text{cm}^2$) covered by a layer of ^{159}Tb ($100 \mu\text{g}/\text{cm}^2$) was prepared by a molecular plating procedure of $^{249}\text{Bk}(\text{NO}_3)_3$ and $^{159}\text{Tb}(\text{NO}_3)_3$ on a $2.77\text{mg}/\text{cm}^2$ Be foil. At the Philips cyclotron of the Paul Scherrer Institute, Switzerland this target was irradiated for about 4 weeks at a beam dose of $3 \cdot 10^{18} \text{ }^{22}\text{Ne}^{6+}$ at a beam energy of $119 \pm 3 \text{ MeV}$ in the middle of the target. ^{176}Re was simultaneously produced in the fusion reaction $^{159}\text{Tb}(^{22}\text{Ne}, 5n)$ and served as a yield monitor for the chemical separation of group 7 oxychlorides. The nuclear reaction products, recoiling from the target were thermalized in He gas loaded with carbon aerosol particles. Adsorbing on the particle surface, they are swept to the remotely controlled OLGA III device. HCl and O_2 are admixed. On a quartz wool plug in the reaction oven of the apparatus held at 1000°C the carbon particles are burned. At the same time the nuclear reaction products form compounds, which are evaporated and separated on-line in the isothermal chromatography quartz column. The retention times of the compounds in the column are mainly dependent on their adsorption interaction with the column surface at the isothermal temperature (Table 1, T_{iso}) and on the carrier gas velocity. The experiment ends for the individual molecule with the decay of the nuclide. Thus, only the species with a longer nuclear lifetime than the retention time pass the chromatography set-up and were subsequently attached to CsCl aerosol particles of a second gas-jet to be transported to the detection device - ROMA. There, the CsCl particles were impacted in vacuum on thin polyethylene foils ($\sim 30 \mu\text{g}/\text{cm}^2$) mounted on the circumference of a stepwise rotating wheel. Every 10 s the gathered samples are successively moved between a series of 12 pairs of PIPS detectors to measure α - and SF-decay in an event-by-event mode with about 70% detection efficiency. ^{176}Re was measured using a HPGE- γ -detector. About 180000 samples were measured during the entire experiment. The overall yield of the complete separation process, from the thermalization of the recoiling fusion products to the sample preparation in the detection device, was determined for ^{176}Re to be about 16%. During the irradiation three different temperatures were adjusted in the isothermal quartz column. Four correlated decay chains, attributed to the decay of ^{267}Bh , were detected at 180°C . At 150°C 2 decay chains were observed. Finally, at 75°C isothermal temperature, where $^{169}\text{ReO}_3\text{Cl}$ still passes the isothermal part of the column with about 80% relative yield, no ^{267}Bh was registered (see Table 1).

Table 1. Detected correlated decay chains related to the decay of ^{267}Bh .

T_{iso} [$^\circ\text{C}$]	Beam dose: $^{22}\text{Ne}^{6+}$	$E_{\alpha 1}$ [MeV]	t_1 [s]	E_2 [MeV]	Δt_2 [s]	$E_{\alpha 3}$ [MeV]	Δt_3 [s]	Decay assignment	N_R
180	$1.02 \cdot 10^{18}$	8.84	26.7	8.35	73.4			$^{267}\text{Bh} \rightarrow ^{263}\text{Db}$ or ^{259}Lr	1.2
		8.72	2.9	8.40	29.9			$^{267}\text{Bh} \rightarrow ^{263}\text{Db}$ or ^{259}Lr	
		8.81	18.4	101/86	16.3			$^{267}\text{Bh} \rightarrow ^{263}\text{Db}$ or ^{259}Lr	0.1
		8.91	10.5	8.37	0.8	8.41	14.6	$^{267}\text{Bh} \rightarrow ^{263}\text{Db} \rightarrow ^{259}\text{Lr}$	0.001
150	$1.00 \cdot 10^{18}$	8.81	24.5	82	21.1			$^{267}\text{Bh} \rightarrow ^{263}\text{Db}$ or ^{259}Lr	0.1
		8.85	34.4	46	98.9			$^{267}\text{Bh} \rightarrow ^{263}\text{Db}$ or ^{259}Lr	
75	$1.00 \cdot 10^{18}$								

$E_{\alpha 1}$ and $E_{\alpha 3}$ represent the α decay energies of ^{267}Bh and ^{259}Lr , respectively.

E_2 indicates the α ($E_2 < 10 \text{ MeV}$) or SF ($E_2 > 30 \text{ MeV}$) decay energy of the indistinguishable in this experiment decay of ^{263}Db ($E_\alpha = 8.35, 8.41 \text{ MeV}$) and ^{259}Lr ($E_\alpha = 8.45 \text{ MeV}$).

t_1 is the life-time of ^{267}Bh from the beginning of the measurement.

Δt_2 shows the life-time of ^{263}Db or ^{259}Lr after the ^{267}Bh decay.

Δt_3 represents the life-time of ^{259}Lr after the ^{263}Db decay.

N_R is the number of random correlations.

Based on the detection of 6 atoms we conclude that Bh behaves like a typical member of group 7 in the periodic table. Bh, similarly to Tc and Re, forms a volatile oxychloride compound, presumably

BhO₃Cl. A careful statistical analysis of the experimental data was applied. The number of random correlations (Table 1, N_R) was evaluated. From the number of detected correlated decay chains, the initial number of ²⁶⁷Bh atoms in the measured samples was determined. Assuming the experimental result at 180°C to be 100 %, the relative yields at 150°C and 75°C were calculated (see Fig.1, filled squares). Assuming the same adsorption process as for TcO₃Cl and ReO₃Cl, using a microscopic model of mobile adsorption [19], first thermodynamic data of element Bh - the standard adsorption enthalpy of BhO₃Cl on a quartz surface - was evaluated: $\Delta H_{\text{ads}}(\text{BhO}_3\text{Cl}) = -75^{+9}_{-6}$ kJ/mol [20]. This value is in a very good agreement with the predictions. Using empirical thermochemical methods different macroscopic properties related to Bh and its compounds have been evaluated. In different chemical systems it was shown that ΔH_{ads} is closely related to the macroscopic volatility of the species. Employing a linear correlation between the microscopic data ΔH_{ads} and the macroscopic data sublimation enthalpy (ΔH_{subl}), which was obtained for the adsorption of chlorides and oxychlorides on quartz surfaces in [21], we estimated from our experimental result $\Delta H_{\text{subl}}(\text{BhO}_3\text{Cl}) = 89 \pm 20$ kJ/mol. Consequently, in agreement with the predictions, BhO₃Cl is supposed to be less volatile than TcO₃Cl ($\Delta H_{\text{subl}} = 49 \pm 12$ kJ/mol) and ReO₃Cl ($\Delta H_{\text{subl}} = 67 \pm 12$ kJ/mol)

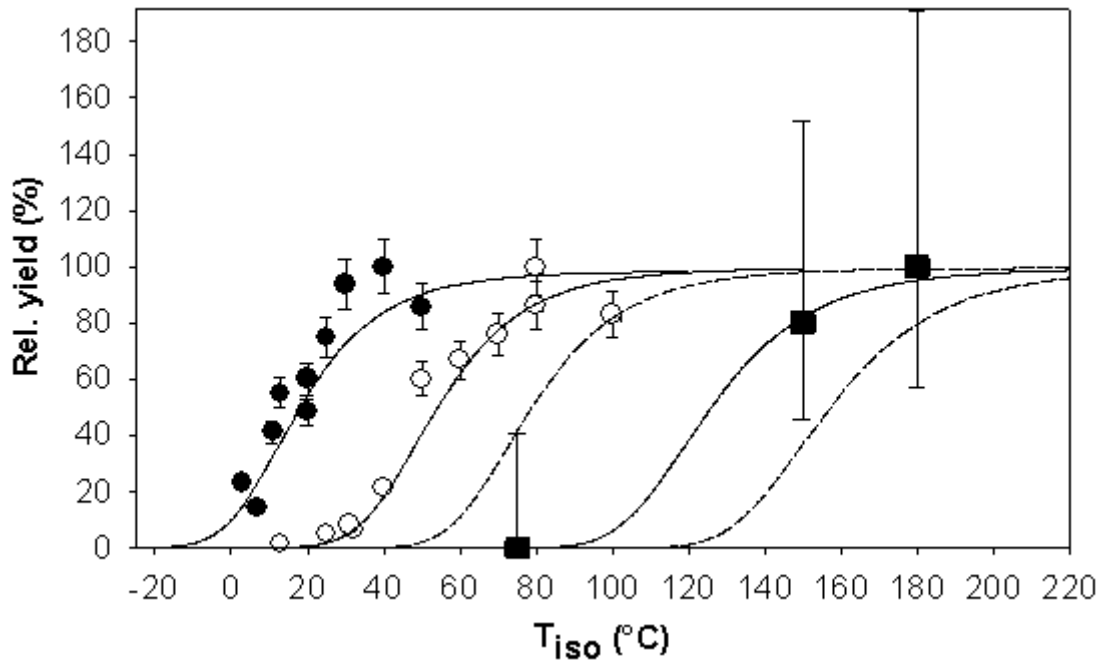


Figure 1. Experimental results of isothermal gas adsorption chromatographic separations in quartz columns. Presented are the relative yields of the compounds ¹⁰⁸TcO₃Cl (filled black circles), ¹⁶⁹ReO₃Cl (open circles) and ²⁶⁷BhO₃Cl (filled black squares, this work) after separation in a OLGA device as a function of isothermal temperature (T_{iso}). The error bars indicate a 68% confidence interval. The lines represent calculated relative yields applying a microscopic model of the adsorption process based on a Monte Carlo approach, with standard adsorption enthalpies of -51 kJ/mol (TcO₃Cl), -61 kJ/mol (ReO₃Cl), and -75⁺⁹₋₆ kJ/mol (BhO₃Cl), respectively.

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Chemical investigations of element 108, hassium (Hs)

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Introduction

The basic aim of chemistry experiments of transactinide elements (TAN) is to establish their place in the periodic table of the elements, i.e. to determine if their chemical behavior is similar to the one of supposed homologs. In this contribution I will try to give an overview of all chemical experiments on element 108, hassium (Hs) that have been reported to date.

Based on the systematics of the periodic table, Hs is expected to be a member of group 8 and therefore homologous to osmium (Os) and ruthenium (Ru). As a member of the transactinide series, its experimental investigation is complicated by low production cross-sections and short half-lives. It has therefore been successfully investigated only recently. Already in the seventies of the last century, several authors mentioned the tetroxides of the two heavier group 8 elements, Ru and Os, to be very outstanding compounds with respect to their unusually high volatility. A possible HsO₄ was considered suitable for isolating Hs from unwanted by-products of the nuclear production reaction [1-4]. While RuO₄ is rather unstable, OsO₄ is well-known to be a stable compound and is widely used in organic chemistry. Recent theoretical calculations on the electronic structure and properties of Hs [5,6] predict the formation of a stable HsO₄ whose properties should be similar to the ones of OsO₄. This is in agreement with an extrapolation of the trend established in group 8 of the periodic table by Ru and Os [7]. All of the reported experiments on the chemistry of Hs therefore aimed at a formation of this compound.

Hs was discovered in 1984, when Münzenberg et al. reported the observation of a correlated decay-chain from ²⁶⁵Hs formed in the nuclear reaction ⁵⁸Fe(²⁰⁸Pb; n) [8]. However, its half-life is only 1.55 ms, too short for a successful chemistry experiment. Early chemistry experiments therefore aimed at the production and detection of more neutron-rich Hs isotopes which were expected to be longer-lived. In some experiments, a nuclide with a higher Z was produced which was expected to subsequently decay to an isotope of element 108. In 1996, ²⁶⁹Hs (T_{1/2}~10 s) was discovered [9], and it was this relatively long-lived isotope which was used in the recent experiments.

In the following, all experiments on the chemical investigation of Hs are presented in a chronological order.

Early experiments

The first attempts to chemically identify elements 108, which had been discovered only one year earlier, were undertaken in Dubna in 1985. Spontaneously fissioning (SF) isotopes produced in the heavy-ion induced fusion reactions ⁴⁰Ar+²³⁵U (leading to ²⁷⁵110 as the compound nucleus, CN) and SF or α -decaying ²⁶⁷Hs produced in the ²²Ne+²⁴⁹Cf reaction (CN ²⁷¹Hs) were searched for [10,11]. ²⁶⁷Hs was believed to have a half-life on the order of 1 s. The nuclear reaction products were thermalized in a Ar/O₂ gas mixture and continuously swept out of the target chamber through a heated CaO filled column which acted as a filter to separate non-volatile transfer products as e.g. actinides, Ra, Fr, and Po. The volatile species were blown onto the surface of a Pb coated Si detector. At the opposite side an annular lavsan track detector was located for registering fission fragments.

In Berkeley, a set-up called the On-line Separation and Condensation AppaRatus (OSCAR) [12] was used for a search for α -decaying ^{272}Hs which was expected to be the electron capture daughter product of ^{272}Mt produced in the reaction $^{254}\text{Es}(^{22}\text{Ne}, 4n)$ [13]. Nuclear reaction products were transported with a KCl gas-jet to the chemistry setup where O_2 was added to the carrier gas. The aerosol particles were caught on a heated quartz wool plug where the transported species were converted to oxides. Non volatile transfer products remained in the reaction area while the volatile oxides were swept out by the gas flow and deposited on a silver disk which was cooled by liquid nitrogen (LN_2). Opposite of the metal disk, an annular Si surface barrier detector was mounted which registered α - and SF decaying nuclides adsorbed on the disk.

In all of these experiments, the decontamination from actinides and other interfering species was excellent. Nevertheless, no events that could be attributed to the decay of Hs were observed and upper limits of 100 pb for the production cross sections of α -decaying nuclides and 50 pb for SF decaying nuclides were established in the Dubna experiments and a limit of 1 nb was reported from the OSCAR experiment. As we know nowadays, the sensitivity of these early experiments was too low to yield positive results. Meanwhile, several isotopes that were unknown at that time were discovered and exhibited decay properties different from the ones assumed (and necessary for a successful experiment).

The IVO-COLD experiment

In 2001, the next attempt to chemically investigate Hs was undertaken by a large collaboration. A schematic of the set-up used is depicted in Figure 1.

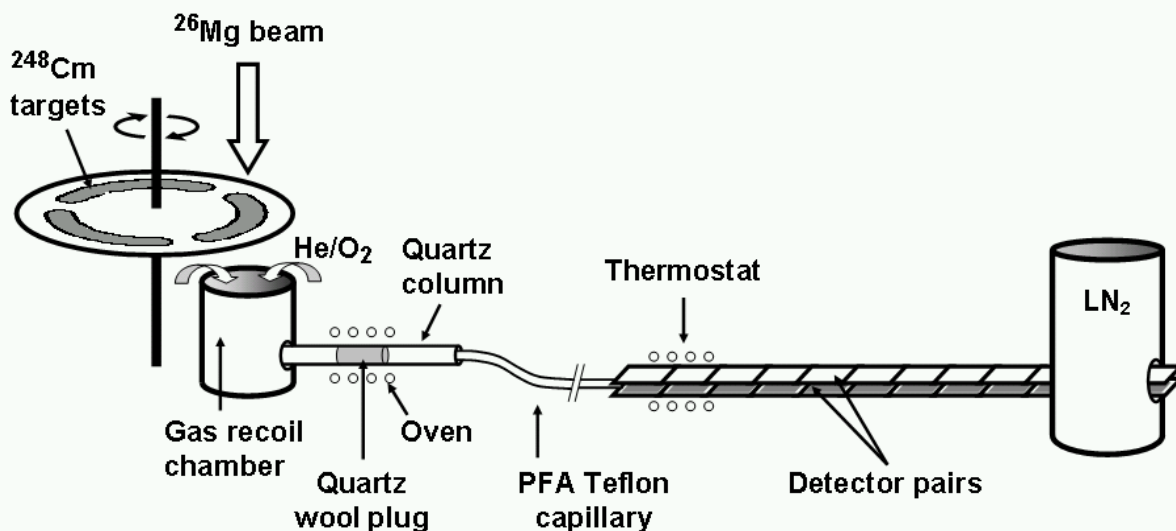


Figure 1. Schematic of the experimental setup in the IVO-COLD experiment. For explanations see text. Adapted from [14].

Relatively long-lived Hs isotopes were produced in the reaction $^{248}\text{Cm}(^{26}\text{Mg}; 5,4n)^{269,270}\text{Hs}$. Reaction products recoiling from the target were thermalized in a gas filled volume called the recoil chamber which was flooded with a He/O_2 mixture. The formed radionuclides were transported by the gas flow to a nearby oven kept at 600 °C where formation of the tetroxide took place. Hs was then transported through a PFA Teflon tube to the detection device in the form of HsO_4 . This technique was named In-situ Voaltization and On-line detection (IVO) [15]. The efficiency of IVO to forward formed short-lived Os

isotopes to the detection system was measured to be 60-90% in test experiments. The method of gas phase adsorption thermochromatography [16] was used to measure the deposition temperature of HsO_4 on the surface of a chromatography column. An on-line thermochromatography system has been developed at Berkeley [17] and an improved version called the Cryo-On-Line Detector (COLD) [14,18] has been built at the Paul Scherrer Institute in Switzerland. The chromatography column consisted of 12 pairs of PIN-diodes (Area: $1 \times 3 \text{ cm}^2$ each) forming a narrow rectangular channel with a spacing of 1.6 mm. PIN-diodes are suitable for registering α -particles and fission fragments. By means of a thermostat and a vessel containing LN_2 , a temperature gradient from -20 to -170 °C was established along the column. Deposition of HsO_4 was expected at a temperature lying between these two values. The overall efficiency of the IVO-COLD system was 30-50%.

Table 1. Observed correlated decay chains. Given are the energies of the observed events and the time difference between an event and the preceding one. The setup used did not allow for determining the lifetime of the mother events. Fission events are marked with an asterisk. Two asterisks identify SF events where only one fragment was registered. n_R is the probability of a chain to be of random origin not related to the decay of a Hs isotope. Det. indicates the detector unit in which the chain was observed. The last column gives the isotope to which the decay chain was assigned to.

#	E_1 [MeV]	E_2 [MeV]	Δt_2 [s]	E_3 [MeV]	Δt_3 [s]	E_4 [MeV]	Δt_4 [s]	n_R	Det.	Isotope
1	9.16	8.66	25.665	94+93*	0.199			$<8 \times 10^{-6}$	2	^{270}Hs
2	9.18	8.69	4.409	8.50	2.365	8.21	55.567	$<2 \times 10^{-6}$	3	^{269}Hs
3	-	8.72	-	53**	3.124			$<2 \times 10^{-4}$	4	$^{269/270}\text{Hs}$
4	8.97	8.64	11.911	94+92*	1.216			$<5 \times 10^{-5}$	4	^{270}Hs
5	9.10	8.68	9.325	94+85*	7.920			$<7 \times 10^{-6}$	3	^{269}Hs
6	8.88	8.90	17.078	8.50	0.846			$<7 \times 10^{-5}$	3	^{269}Hs
7	9.14	-	-	108**	42.615			$<4 \times 10^{-4}$	3	$^{269/270}\text{Hs}$

Data was acquired during 64.2 h and a total of 10^{18} particles passed through the target. The obtained α -spectra were very clean and exhibited only α -particle lines of ^{211}At and $^{219,220}\text{Rn}$ and their daughters. ^{219}Rn was added to the carrier gas to allow for an on-line calibration of the detectors. The correlation analysis revealed a total of seven correlated decay chains [19] which are given in Table 1. The distribution of Hs and Os in the temperature gradient tube is shown in Figure 2 which contains the merged thermochromatogram of $^{172}\text{OsO}_4$ ($T_{1/2}$: 19 s) and the events attributed to the decay of a Hs isotope.

The enthalpy of adsorption ΔH_{ads} of the species on the column surface material (silicon nitride, Si_3N_4) was extracted from the measured deposition distribution by using Monte Carlo simulations of the trajectories of single molecules as they move along the column under real experimental conditions [20] (see Fig. 2, solid lines). The only free parameter is the ΔH_{ads} of the compound on the stationary phase. The half-life of the nuclide is a crucial parameter in this procedure and since it has not yet been measured for ^{270}Hs , the ΔH_{ads} of the compound on the silicon nitride surface was evaluated using only the three decay chains attributed to ^{269}Hs which occurred in detector pair 3. Values of $\Delta H_{\text{ads}} = (-46 \pm 2) \text{ kJ/mol}$ (68% c.i.) for HsO_4 and $(-39 \pm 1) \text{ kJ/mol}$ for OsO_4 were deduced using a $T_{1/2}$ value of $(11^{+15}_{-4}) \text{ s}$ [9,21] for ^{269}Hs . This result points to HsO_4 as the transported species. The ΔH_{ads} value of OsO_4 of $(-39 \pm 1) \text{ kJ/mol}$ deduced from this experiment was in good agreement with earlier investigations using quartz surfaces [1,15,17].

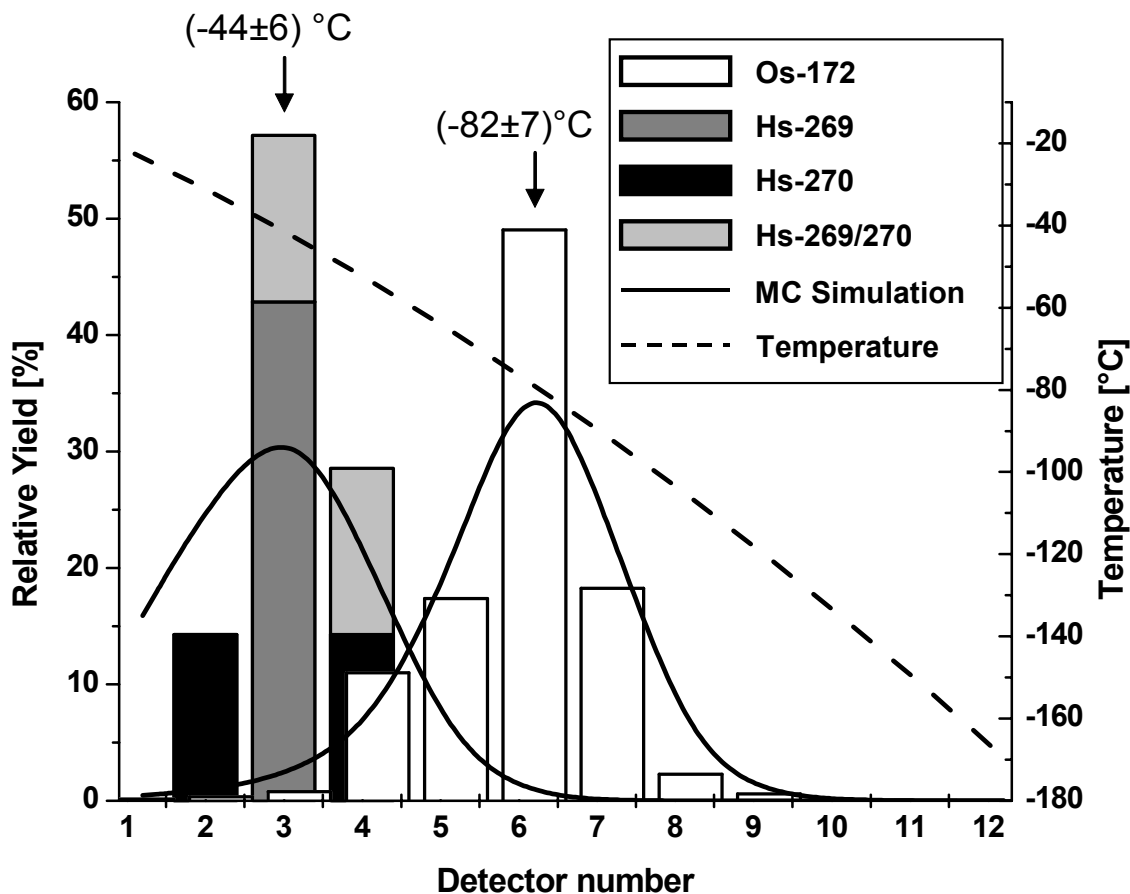


Figure 2. Merged thermochromatogram of HsO_4 and OsO_4 [14]. The deposition temperatures are indicated. Solid lines represent results of a Monte Carlo simulation. The dashed line indicates the temperature gradient. Adapted from [14].

The CALLISTO experiment

The most recent Hs experiment has been performed by a GSI - Univ. Mainz - JAERI collaboration. The setup used was named Continuously working Arrangement for for clusterLess transport of In-SiTu produced volatile Oxides (CALLISTO) [22] and is depicted in Figure 3. The goal of the experiment was the deposition of the volatile HsO_4 on a reactive substrate. OsO_4 is known to react with hydroxides forming osmates(VIII) of the composition $[\text{OsO}_4(\text{OH})_2]^{2-}$ and test experiments at GSI showed that carrier-free OsO_4 deposits on hydroxide surfaces with high yields [23]. Hs was produced using the same nuclear reaction as the IVO-COLD experiment, i.e. $^{26}\text{Mg}(^{248}\text{Cm}; 5,4n)^{269,270}\text{Hs}$. These isotopes were converted to HsO_4 immediately behind the target and transported to the chemistry device with the gas flow. HsO_4 was deposited on a thin layer of NaOH, presumably due to reduction according to $2\text{NaOH} + \text{HsO}_4 \rightarrow \text{Na}_2[\text{HsO}_4(\text{OH})_2]$, yielding a hassate(VIII) [24]. The detection system consisted of a narrow rectangular channel with the bottom coated with a thin-layer of NaOH. The top consisted of PIN-diodes allowing for registering α -particles and fission fragments in a 2π -geometry. A total of 4 of these detector boxes were available. Three were serially coupled while the fourth one was available for maintenance and coating.

The present status of the data analysis shows that formed HsO_4 was deposited on the first few centimeters of the NaOH covered channel. The preliminary results indicate one correlated α - α - α -decay chain and 5 α -SF chains which were attributed to the decay of a Hs isotope [25]. The distribution of the 6 decay chains in the detection system is similar to the one observed for Os. Thus, it appears likely that Hs reacts with the NaOH surface in a similar way as Os.

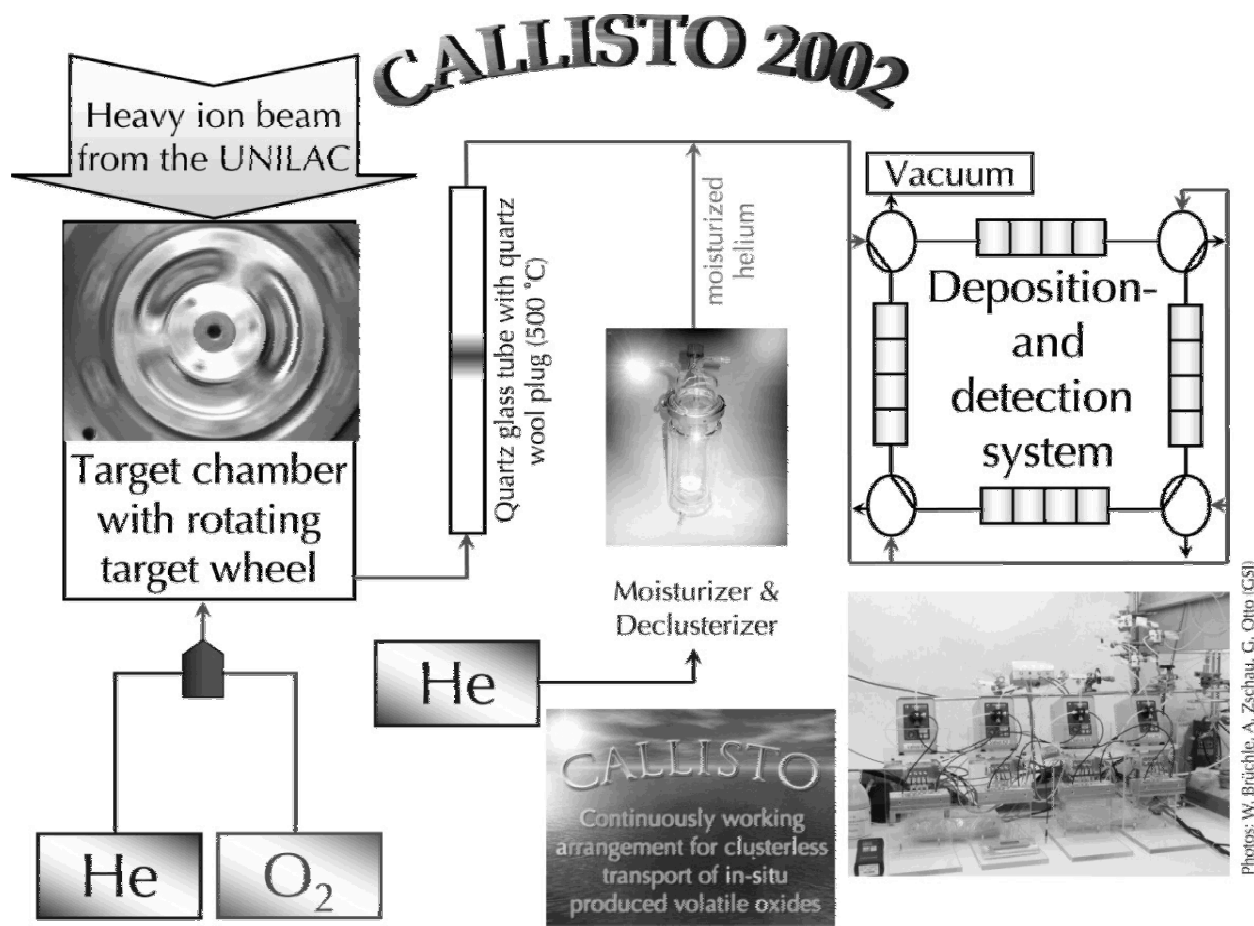


Figure 3. The CALLISTO setup [22]. For details see text. Figure courtesy of A. v. Zweidorf.

Conclusions

Currently, two experiments have successfully investigated the chemical behavior of Hs. In the first study, formation of a volatile oxide, presumably HsO_4 and its deposition on a dielectric surface was studied. It was found that the interaction was slightly stronger for HsO_4 than OsO_4 . Nevertheless, the findings justified the classification of Hs into group 8 of the periodic table. In the second experiment, the reaction of HsO_4 with a NaOH surface was investigated and evidence for the formation of a hassate(VIII) was obtained. Therefore, Hs has revealed an analogous behavior to Os also in this system.

Acknowledgment

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Chemical properties of element 112

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Introduction

Study of chemical properties of element 112 (E112) are of great interest in itself. In addition, they can provide an independent determination of its atomic number and decay properties. E112 has been obtained directly in the $^{238}\text{U} (^{48}\text{Ca}; 3n)$ reaction [1] and also as the daughter of element 114 produced in the $^{242,244}\text{Pu} (^{48}\text{Ca}; 3(4)n)$ reaction [2,3]. The isotope $^{283}112$ with a 3-min half-life decaying by spontaneous fission (SF) [1] is a very attractive nuclide for a first chemical identification in the super heavy element (SHE) region. According to its predicted ground state electronic structure, E112 belongs to group 12 of the Mendeleev Periodic System (MPS), and is the nearest homologue of Hg. Based on classical extrapolations, E112 should form stronger bonds with surfaces of some metals, than the bonding between E112 atoms in the hypothetical metallic phase [4]. Chemical studies of E112 might reveal strongly pronounced "relativistic effects" that are theoretically predicted. The expected enhanced volatility of E112 makes it an ideal object for the study of its elemental state chemical behavior by gas-phase chemical methods. The strong interaction with suitable metallic surfaces at ambient or even below-ambient temperatures opens up good prospects for using modern semiconductor detectors for on-line detection of volatile SHE on a one-atom-at-a time level. The calculations and prognoses made for E112 predict a weaker interaction with Au and a higher volatility than that of its lighter homologue Hg [5,6]. At the same time, relativistic quantum chemistry predicts increasingly strong "relativistic effects" in the chemistry of super-heavy elements [7,8]. The calculated contraction stabilizes the spherical s and $p_{1/2}$ electron orbitals, which more efficiently shield the nuclear charge and thus destabilize the $p_{3/2}$ - and d - orbitals. This may strongly influence the chemical behavior of the $7s$ and $7s7p_{1/2}$ elements, E112 and E114. They are predicted to approach the behavior of noble gases in volatility and chemical inertness [9]. Therefore, one has to investigate the volatility and adsorption behavior of E112 concurrently with those of Hg and Rn.

The chemical study of element 112 in Dubna

As a first approach in January 2000 [10], performed in Dubna, an international team tried to detect an "Hg-like" behavior of E112, by assuming that it should strongly adsorb on gold surfaces at ambient temperature. The reaction products were transported from a recoil chamber through Teflon capillary 30 m in length by helium. This transportation method was also a very good chromatographic separation – only very volatile species could reach the detector. The detector consists of 8 chambers in series, placed in an assembly of 86 neutron counters. In the each chamber were two detectors (2x2 cm) covered with thin gold layers, the distance between the top and bottom detectors was 1 mm. More than 95% of ^{185}Hg was deposited in the first chamber. During the 10 days of bombardment an integral dose of $6.85 \cdot 10^{17}$ was collected. However, no SF events were registered. Thus, the first experiment did not provide an answer as to the physical and chemical properties of element 112. The second experiment was performed at the FLNR JINR in November/December 2001 [11]. The experimenters had to increase by several times, the beam dose to detect E112 atoms in both, the adsorbed state or the gaseous phase. For this purpose, a special flow-through ionization chamber was designed to register SF-decays in the gaseous phase. Figure 1 shows a basic schematic of the setup. As in the first experiment, a $\sim 2 \text{ mg/cm}^2$, 20 mm in diameter $^{238}\text{U}_3\text{O}_8$

target (2), containing 100 μg of ^{147}Nd was deposited on a 2 μm HAVAR foil. It also served as a vacuum window and was supported by a thick water-cooled Cu grating (3) with a transparency of 80%. The recoils were thermalized in pure helium and transported through a 25 m long PTFE capillary to detectors situated behind a concrete wall, which served as a shield against radiation from the cyclotron. The first detector assembly (6) was a circular chamber with 8 pairs of PIPS detectors with a working area of 18×18 mm^2 each, covered with 30 $\mu\text{g}/\text{cm}^2$ Au. The gap between the "top" and "bottom" detectors was 1 mm (Fig. 2a). The gas exiting the chamber (6) was mixed with appropriate quantities of argon and methane, then passed through an aerosol filter into the ionization chamber (7), see Fig. 2b. Both detection chambers were mounted in an assembly of 126 ^3He -filled counters (8), which registered fission neutrons with an efficiency of about 35%. Discriminated pulses from the PIPS detectors and the ionization chamber triggered measurement of fission neutrons. In the latest experiment the beam energy in the middle of the target layer was 234 MeV. After 22.5 days of bombardment, an integral beam dose of $2.8 \cdot 10^{18}$ of ^{48}Ca ions was accumulated.

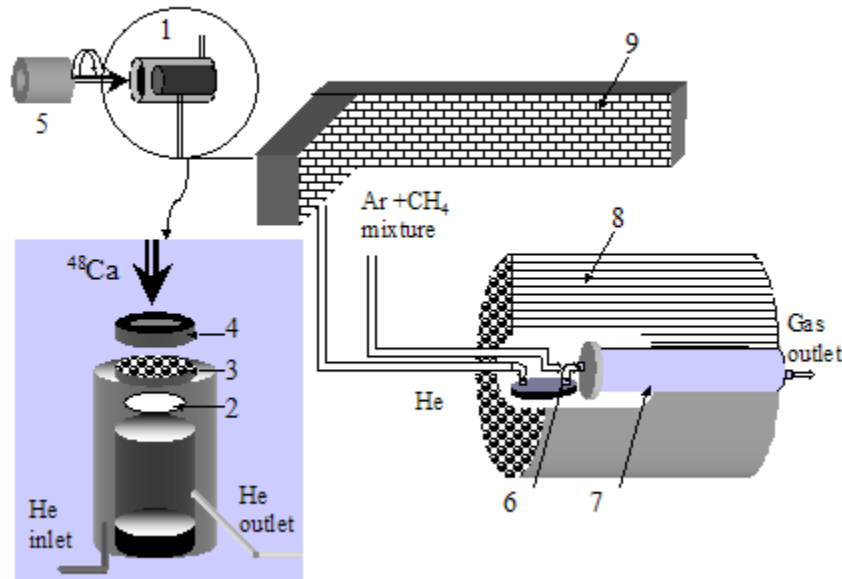


Figure 1. Schematic view of the experimental setup: 1 – recoil chamber; 2 – ^{238}U target; 3 – Cu grating; 4 – Cu collimator; 5 – wobbler device; 6 – circular chamber with 8 pairs of PIPS detectors; 7 – ionization chamber; 8 - assembly of 126 ^3He neutron counters; 9 – concrete shielding wall.

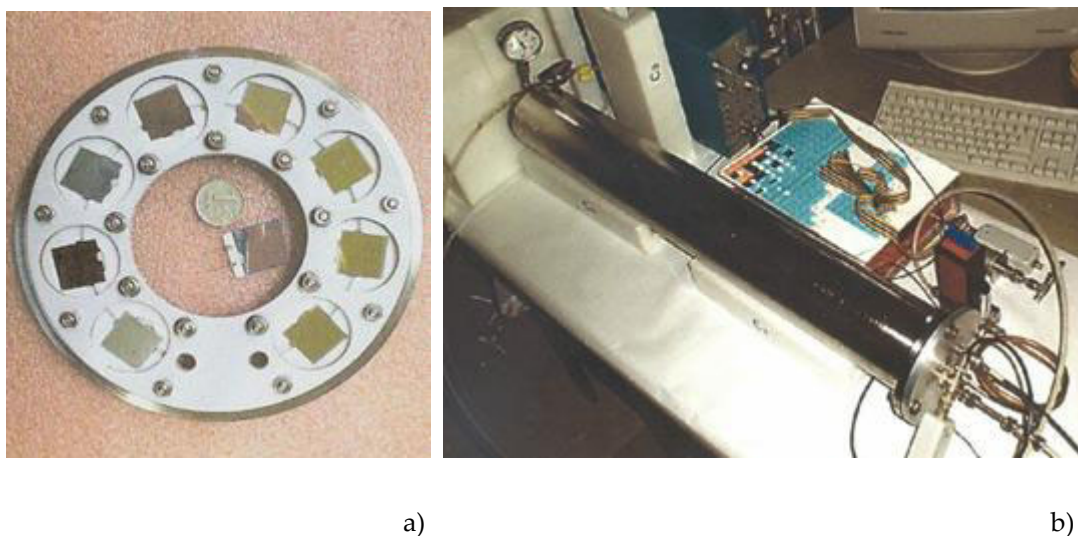


Figure 2. View of the open PIPS detector assembly* (a) and ionization chamber (b).

*Only 8 bottom detectors mounted in the PTFE disks are shown.

The top detectors, gas inlet and outlet, as well as covers are removed.

The behavior of Hg and Rn atoms in the PIPS detector assembly was traced by registering the α -decays of ^{185}Hg ($T_{1/2} = 49$ s) and ^{220}Rn ($T_{1/2} = 55$ s), which were produced in the fusion reaction $^{\text{nat}}\text{Nd}(^{48}\text{Ca};\text{xn})$ and in transfer reactions $^{238}\text{U}+^{48}\text{Ca}$. More than 95% of ^{185}Hg atoms were adsorbed already in the first pair of PIPS detectors. In contrast to this, only a minute part of ^{220}Rn nuclei decayed within this detector assembly, practically uniformly over all the 8 pairs of PIPS detectors. Under the experimental conditions, no known volatile species of heavy actinides or light transactinides could be formed. Gamma spectra measurements and comparison of long-living α -activities in the recoil chamber and on PIPS detectors yielded a gaseous element purification factor of $5 \cdot 10^5$. Non-volatile species could reach the detectors only by aerosol transportation. The aerosol filter installed between the PIPS detector assembly and the ionization chamber increased the factor of purification from non-volatile products by 10^4 . No signals corresponding to the energy release higher than 12 MeV came from the PIPS detectors, i.e. no SF event were detected. In the ionization chamber 8 spontaneous fission events were registered in coincidence with prompt fission neutrons. During 100 days of background measurements with the ionization chamber before and after the experiment, 4 signals were detected in the fission fragment energy range. From these data, the 95% confidence interval for the events counting rate is $7^{+7.0}_{-4.4}$. Assuming an overall procedure efficiency of 40% the effective production cross section of $^{283}112$ in the reaction $^{238}\text{U} + ^{48}\text{Ca}$ was calculated to be $2^{+2.0}_{-1.2}$ pb. Using a model of mobile adsorption, for the description of migration velocity of species in chromatographic column, and a Monte Carlo simulation, the authors evaluated the adsorption enthalpies of Rn to be: $-\Delta H_{\text{ads}}(\text{Rn}) \approx 36$ kJ/mol and from the estimated upper limit of the retention time of E112: $-\Delta H_{\text{ads}}(112) \leq 60$ kJ/mol. Thus, in the atmosphere of an inert gas, the atoms of E112 showed enhanced volatility and did not form strong metal-metal bonds when hitting the Au surface – E112 behaves more like the noble gas Rn rather than Hg. Such marked difference in the chemical properties of the transactinide E112 and its nearest homologue Hg was demonstrated for the first time. Undoubtedly, the next step is a quantitative comparative study of physical-chemical properties of Hg, Rn and E112. This experiment was performed in Darmstadt in spring of this year.

Comparative study of Hg, Rn and element 112 using COLD cryo-detector

In the third experiment the same technique was used, that was earlier developed for chemical experiments with element 108, hassium [12,13]. The principal distinction from two previous experiments was detection of Hg, Rn and element 112 in the same thermo-gradient detector. It opened the possibility for comparative quantitative study of these elements. The set-up involves a ^{238}U target (medial thickness 1.6 mg cm^{-2}) on a rotation wheel bombarded with up to $1 \cdot 10^{12}$ $^{48}\text{Ca}^{7+}$ particles per second, supplied by the UNILAC accelerator at the Gesellschaft für Schwerionenforschung mbH (GSI). The 346 MeV beam delivered by the UNILAC, after passing through a medial 3.7 mg cm^{-2} Be vacuum window and a medial 2.2 mg cm^{-2} backing-foil (Be) resulted in a ^{48}Ca projectile energy of around 222 – 239 MeV inside the ^{238}U target. Products of the heavy ion induced nuclear fusion reaction recoiling backwards out of the target were thermalized in dried 1 l/min He carrier gas. The inner surface of the newly designed recoil chamber was completely covered by a quartz insert to inhibit an adsorption of a potentially metallic E112 on its metal surfaces. Only gaseous products are swept out of the recoil chamber through an open quartz column. Subsequently, they are transported to an oven with a quartz wool filter heated to 850°C . Aerosol particles produced by beam induced sputtering in the target material and from the beam dump are stopped in this filter. Ultimately, separation factors of about 10^7 have been measured for non-volatile species. The volatile products pass this filter and a connected 10 m long PFA-capillary to a Ta-Ti-getter heated up to 1000°C . Trace amounts of water are removed from the carrier gas by this getter. Subsequently, the remaining gaseous products enter the COLD [14] – cryo on-line detector – thermo chromatography column. COLD establishes a negative temperature gradient from $+35^\circ\text{C}$ to -187°C (see Fig. 3). The new version of this device consists of 32 silicon PIN-photodiodes with $10 \times 9.8 \text{ mm}^2$ active area mounted in a row at a distance of 1.6 mm opposite to an Au surface and forming a rectangular gas chromatographic column. α - or SF-decays from atoms adsorbed on the Au surface were detected with 2π -detection geometry. Au layer was selected as chromatographic surface to distinguish, if possible, between metallic and non-metallic properties of E112. Similar to Hg, the formation of a metal bond with the Au surface is expected for a metallic E112 [15]. Furthermore, chemical inertness of Au to oxidation provides a clean metallic chromatographic surface. The over-all-efficiency detecting a fission fragment generated from a mother isotope adsorbed on the detector array was 77 %. The whole detector set-up is placed into a vacuum tight steel box under low pressure to isolate it thermally and to eliminate the moisture from the surrounding air. The experiment to produce E112 lasted 17.08 days during which a total of around $2.8 \cdot 10^{18}$ ^{48}Ca particles passed through the target. For continuous verification of the IVO-COLD-system one of the three banana shaped segment of the $^{\text{nat}}\text{U}_3\text{O}_8$ target contained $21.7 \text{ } \mu\text{g cm}^{-2}$ $^{\text{nat}}\text{Nd}$ for producing $^{182-185}\text{Hg}$ in the nuclear reaction $^{\text{nat}}\text{Nd}(^{48}\text{Ca}, 8n)$. The Hg-isotopes deposited completely on the Au-surface opposite the first five detectors (see Fig. 3). In the reaction of ^{48}Ca on ^{238}U , different Rn-isotopes were produced as transfer products and transported to COLD. $^{219-221}\text{Rn}$ and their daughters decays were a second parameter to check the proper functioning of the system, as they were – according to their half-lives – adsorbed on the last 4 detectors of the cold end of the chromatography column (Fig. 3). During the entire experiment 13 fission events above 35 MeV (incorrect energy calibration) were observed. In the background measurement at the GSI – lasting 24 days – 5 fission events above 35 MeV were detected. No indications for actinides and other non volatile transfer reaction products, which could be transported by aerosol particles through the whole setup were observed during the experiment and in the subsequent background measurement. The result shows evidence for the observation of a spontaneous fissioning isotope $^{283}112$, which is extremely volatile in elemental state and accumulates at temperatures below -160°C on the last detectors. The final data analysis is in progress.

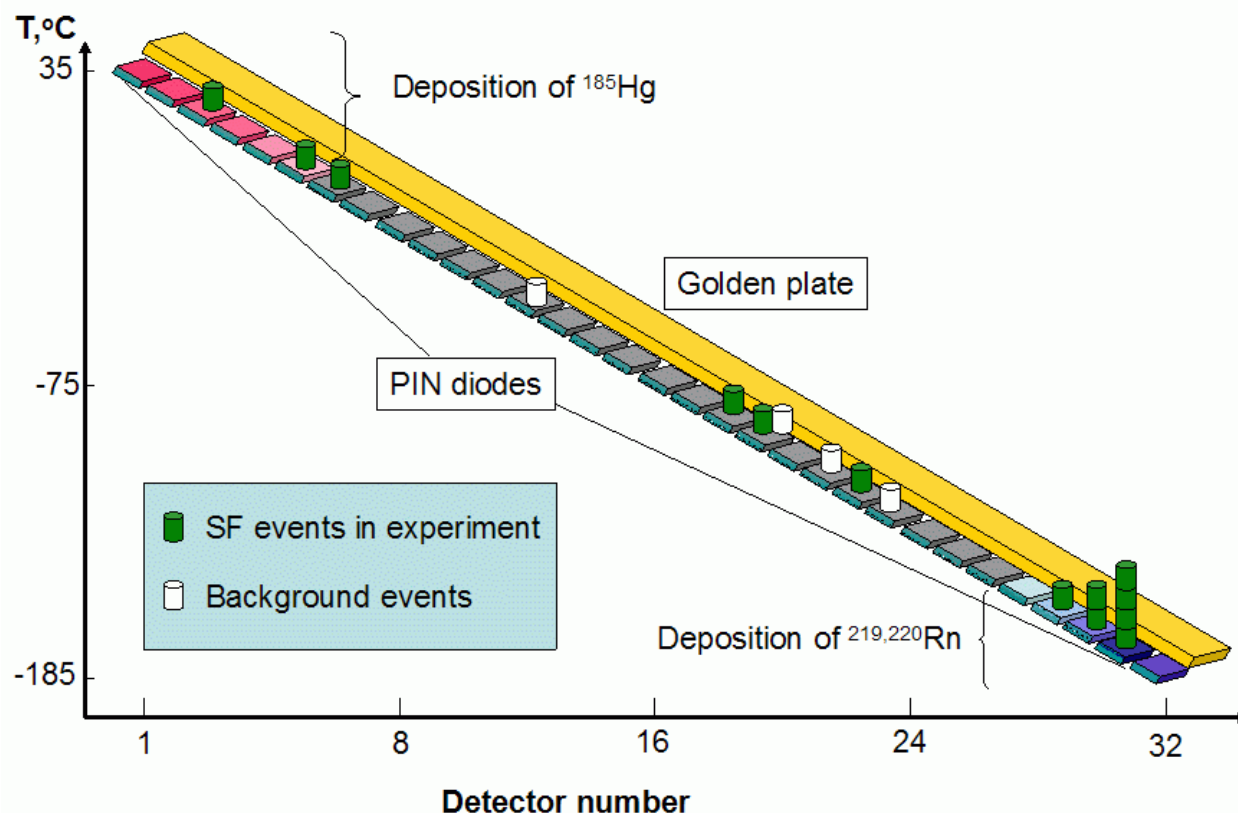


Figure 3. Schematic of the detector and distribution of Hg, Rn and SF events.

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Anion-exchange behavior of rutherfordium and dubnium in pure HF solution

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Many attempts have been made to study the aqueous chemistry of element 104, rutherfordium, and element 105, dubnium [1]. Differences in the complex formation among Rf, Db and their lighter homologues were deduced from some of the experiments, and some yielded conflicting results [1]. Although several experiments for Rf and Db in various HF solutions have been performed [2-5], enough data have not been accumulated to discuss in detail the fluoride complexations and/or relativistic effects. In the present work, we have investigated the chemical behavior of Rf and Db together with their group-4 and group-5 homologues by an anion-exchange chromatography in pure HF solution expected to be a fast and simple reaction mechanism to form anionic complexes.

The isotopes ²⁶¹Rf, ⁸⁵Zr, and ¹⁶⁹Hf were produced in the ²⁴⁸Cm(¹⁸O,5n), ^{nat}Ge(¹⁸O,xn), and ^{nat}Gd(¹⁸O,xn) reactions, respectively, at the JAERI tandem accelerator [6]. On-line anion-exchange separations for Rf, Zr, and Hf in 3.9-13.9 M HF solutions were performed using the Automated Ion exchange separation apparatus coupled with the Detection system for Alpha spectroscopy (AIDA) [7]. AIDA enables us to perform cyclic discontinuous chromatographic separations in aqueous phase and automatic detections of α -particles within a typical cycle time of 1 - 2 min. The reaction products recoiling out of the target were transported by the He/KCl gas-jet system to AIDA, and were dissolved with 240 μ L of 3.9 to 13.9 M HF and fed into an anion-exchange column (MCI GEL CA08Y, 1.6 mm i.d. \square ~7.0 mm) at a flow rate of 0.74 mL/min. Figure 1 shows typical elution curves of short-lived ⁸⁵Zr and ¹⁶⁹Hf in 14 M HF solution. These elution curves exhibit a good performance of the present anion-exchange separation system, expecting that the chemical equilibrium is established. The effluent was collected on a Ta dish as Fraction 1 and evaporated to dryness with hot He gas and a halogen heat lamp. The products remaining in the column were eluted with 210 μ L of 4.0 M HCl. This effluent was collected on another Ta dish and evaporated to dryness as Fraction 2. Each pair of Ta dishes, Fractions 1 and 2, was automatically transferred to the α spectrometry station equipped with the eight 600 mm² PIPS detectors. Figure 2 shows typical α particle energy spectra for Fractions 1 and 2. From the activities A_1 and A_2 observed in Fractions 1 and 2, respectively, the percent adsorption (%ads) on CA08Y was evaluated by the equation: %ads = 100 A_2 /(A_1 + A_2). The %ads values of Rf, Hf and Zr in the various concentrations of HF are shown in Figure 3. This result shows a notable difference in the sorption behavior between Rf and its homologues Zr and Hf. The %ads values of Zr and Hf are in good agreement with each other and both decrease steeply with an

increase of the HF concentration above 8 M. Although the %*ads* of Rf also decreases with the HF concentration, the values are apparently smaller than those of Zr and Hf, suggesting that the fluoride complexing strength of Rf is weaker than that of Zr and Hf.

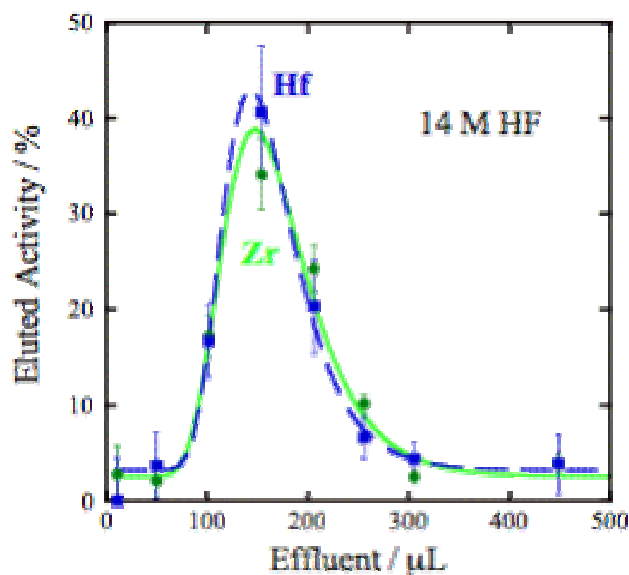


Figure 1. Elution curves for ^{85}Zr and ^{169}Hf in 14 M HF from an anion-exchange column (MCI GEL CA08Y, 1.6 mm i.d. $\square \sim 7.0$ mm) at a flow rate of 0.74 mL/min.

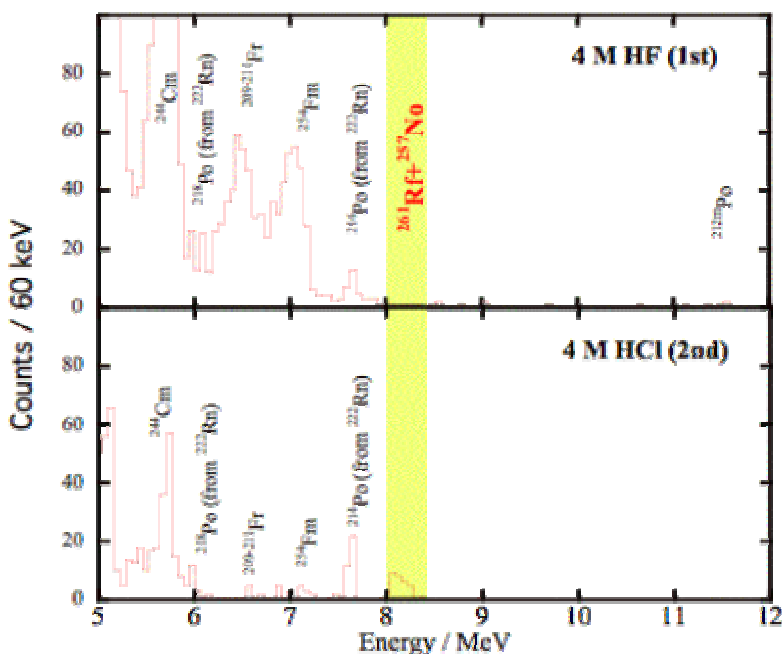


Figure 2. α -particle energy spectra of two eluted fractions: (upper) 4 M HF and (lower) 4.0 M HCl.

On the other hand, we are also interested in a fluoride complexing strength of Db and its group-5 homologues, Nb and Ta, and pseudo-homologue Pa on the anion-exchange resin. The sorption sequence of $\text{Ta} \geq \text{Nb} \gg \text{Pa}$ in 2-15 M HF solutions was observed in the batch experiment, and the %*ads* value of Db

together with Ta in a 14 M HF solution was investigated. ^{262}Db and ^{169}Ta were produced in the $^{248}\text{Cm}(^{19}\text{F}, 5n)$ and $^{147}\text{Sm}(^{19}\text{F}, xn)$ reactions, respectively, at the JAERI tandem accelerator [6]. 1702 anion-exchange separations were conducted using AIDA with a small column of 1.0 mm i.d. \times 3.5 mm. It was found that the %ads value of Db is smaller than that of Ta, suggesting that the sequence of the fluoride complexing strength is $\text{Ta} \geq \text{Nb} > \text{Db} \geq \text{Pa}$.

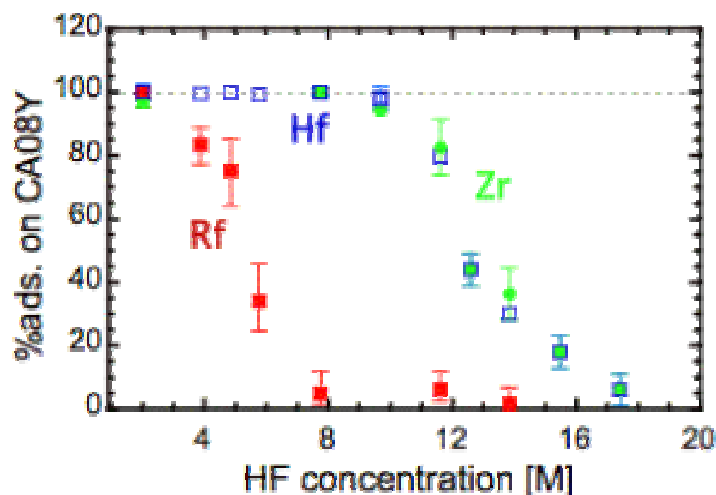


Figure 3. Variation of the percent adsorption (%ads) of Zr, Hf, and Rf on CA08Y as a function of the HF concentration.

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Current status of transactinide research with the liquid-liquid extraction system SISAK

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Introduction

SISAK^a is a fast, chemical-separation system for liquid-liquid extraction. It was developed to investigate short-lived nuclides recoiling out of an irradiated target and transported in a gas jet. The system is based on small centrifuges with a continuous feed and output [1-3].

During recent years, work has been undertaken to deploy SISAK in studies of the chemical properties of the transactinide elements ($Z \geq 104$) [4-8]. The only suitable detection method found was liquid-scintillation (LS) detection [9]. This was mainly because of the rather high flow rates (0.5-2.0 mL/s) encountered in the SISAK system. Other detection methods usually require either thin, dry samples or very thin liquid films. No suitable method was found to prepare such samples without an unacceptable time delay between separation and detection.

In 2000 the first successful transactinide experiment [5] with SISAK was performed at the Lawrence Berkeley National Laboratory (LBNL) in Berkeley, USA. In this experiment it was proved that it was possible to extract and detect the transactinide ²⁵⁷Rf with SISAK. The ²⁵⁷Rf activity was produced with a 235 MeV ⁵⁰Ti¹²⁺ beam from the LBNL 88-inch cyclotron hitting a rotating ²⁰⁸Pb target. The recoils from the target were then separated in the Berkeley Gas-filled Separator (BGS) and transferred to the chemistry apparatus in a gas jet. The pre-separated recoil products were transferred from the BGS to the gas jet by using a unique Recoil Transfer Chamber (RTC), then recently constructed by Uwe Kirbach.

After the successful transactinide pilot-experiments in 2000 and 2001 with the BGS, work was undertaken in Oslo to develop suitable extraction systems to make detailed investigations of the chemistry of Rf. The first stage of this investigation was detailed checks on the reproducibility of the SISAK system, i.e. how accurate measurements are possible using such an on-line extraction system? As is reported below, this showed that several chemical systems thought to be usable with the SISAK system could not be used due to problems with sorption on or in the construction material of the SISAK centrifuges.

The second stage of the mentioned investigation was to develop the chemical extraction system to be used in future Rf experiments. This work is reported in a separate extended abstract to the TAN'03 conference and will be presented as a poster at the conference (Darina Poláková and co-workers).

In parallel to the work on the chemistry to be used in the SISAK system, work has been performed in Oslo to improve the performance of Liquid Scintillation (LS) detection system and to improve the acquisition and analysis methods. LS counting has high efficiency, but suffers from relatively poor energy resolution (about 300-keV FWHM at 7-MeV α energy) and is sensitive to β -particles and γ -rays. This puts very stringent demands on the detection system, because most of the β - and γ -emitting contaminants are produced with orders of magnitude higher yield than the transactinide under study. Therefore, further improvements to the SISAK detection system have been pursued. This work is also reported in a separate extended abstract and will be presented as a poster at the conference (Liv Stavsetra and co-workers).

The SISAK system as an analytical tool

If the SISAK system is to be used for detailed chemical studies of transactinide elements, then it is paramount to know the precision at which distribution ratios can be measured. The distribution ratio for a given element is its concentration in the organic phase divided by its concentration in the aqueous phase. The most obvious limit to the precision of which such values can be measured is of course the uncertainty due to counting statistic. The largest relative uncertainty will dominate the uncertainty for the distribution ratio. At high distribution ratios, $D > 100$, or low distribution ratios, $D < 1/100$, less than 1% of the activity will be in one of the phases. Therefore, in situations where limited amounts of activity are available, the amount of activity in this phase is practically impossible to determine. In addition to this, and even more significant, one has the practical problem of achieving perfectly clean phases. Thus, if the phase separation is not perfect and traces of the wrong phase are carried with the one with the least amount of activity, serious errors might result. Therefore, distribution ratios between 1/10 and 10 is the safest range to work in when only small amounts of activity are available. This is a typical situation in a transactinide experiment. For experiments with the transactinide's homologues, the activity is available in larger amounts and one can typically extend the range to between 1/100 to 100.

For rutherfordium experiments an extraction system based on extraction from high concentration nitric acid (2-6 M) with dibutyl-phosphoric acid was originally developed [4]. The distribution ratio for Hf was measured at many different installations and at different times with this system. After a while it became clear that the results varied much more than could be attributed to counting statistics. This was worrying, as it either meant there was a very large entrainment of the wrong phase, or some other property of the SISAK system interfered with the measurements. Therefore, a detailed investigation of this effect was initiated at the beginning of 2002. The parameters investigated were: Flow rate and flow-rate ratio of the phases, rotation speed of the centrifuge, temperature of the phases, and sensitivity to reaction rates. The latter might be important because the mixing and separation of the phases are too fast to reach equilibrium conditions, thus variations in closeness to equilibrium might be important. Experiments at the Oslo Cyclotron Laboratory soon showed that neither of these parameters were to blame, but the large variation of the distribution ratios persisted. It became evident that the variations seemed to be a function of the time the system had been in contact with the aqueous phase (> 1 M nitric acid). This indicated interference with the centrifuge construction-material (PolyEtherEtherKetone, PEEK) or tubes (made of PerFluoroAlkoxy, PFA) of the system. This problem is illustrated in Fig. 1, where the distribution ratio is plotted as a function of the sum of activity in the two phases (compared to how much activity enters the centrifuge). As can clearly be seen, there is a large loss of activity. Furthermore, when more activity is retained in the centrifuge, the distribution value increases. This is because mainly the aqueous phase activity is retained, not the activity extracted into the organic phase.

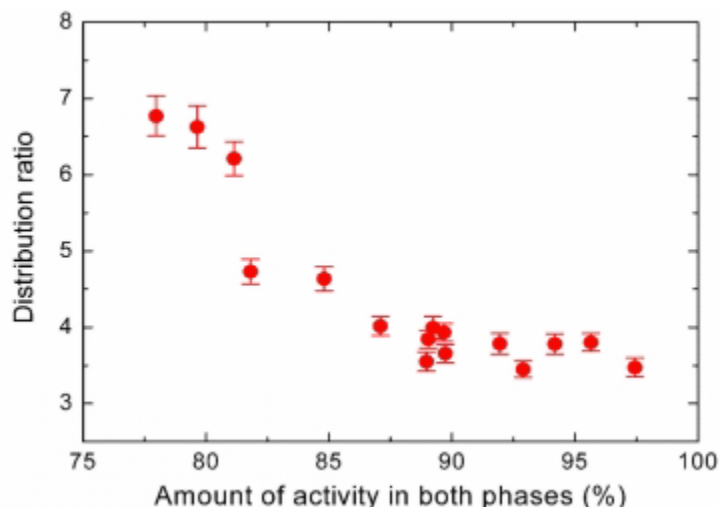


Figure 1. Comparison between the amount of ^{169}Hf activity at the centrifuge outlets and the distribution ratio between activity in the two phases.

First it was suspected that the PFA tubes were at fault, thus they were changed with PEEK tubes. However, this made the problem even worse. Therefore, it could be concluded that the PEEK acted as a sort of chromatography column, retaining at least one of the aqueous phase species. This was a surprising result, as the PEEK construction-material was selected due to its ability to withstand strong acids, among them nitric acid. Unfortunately, there obviously is a significant difference between being resistant and inert. In the case of the nitric acid the PEEK acts much like a sponge.

On basis of these findings, a search for a more suitable system to study the chemistry of rutherfordium was undertaken. In addition, such a system was required to differentiate between Zr and Hf. This is necessary as it is of interest to classify the chemistry of rutherfordium as either Zr- or Hf-like, or to be able to point out certain trends in the extraction of Zr, Hf and Rf. This can not be done if they all extract with more than 90% yield. As reported in one of our other TAN'03 contributions (Poláková and coworkers), such a system has been developed.

The future: SISAK after shutdown of the 88-inch LBNL cyclotron

The BGS coupled to the 88-inch LBNL cyclotron was a very good tool for producing transactinide activity for SISAK. Unfortunately, the cyclotron is being shut down. Hopefully, a similar facility will be established at the Gesellschaft für Schwerionenforschung (GSI) in Darmstadt, Germany. Until then, SISAK has to utilize other methods to remove unwanted activity from the product stream. A general method would be to insert a chemical cleaning-stage in front of the centrifuge used to study the extraction chemistry of a given element. This can be done by adding two additional centrifuges for extraction/back-extraction, as illustrated in Fig. 2. Such systems have been developed for a number of extraction systems, see e.g. [10], but needs to be developed for the TOA/sulphuric acid system described by Poláková and coworkers.

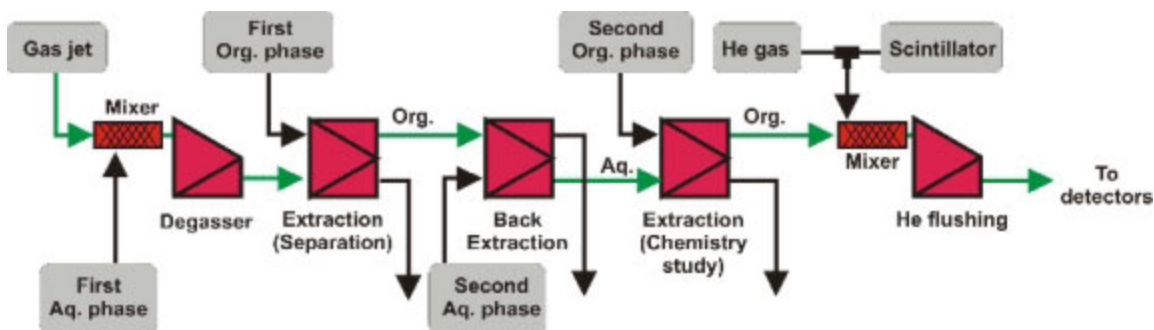


Figure 2. Schematic drawing of a three stage SISAK system which first removes unwanted activity by an extraction/back-extraction section and then have a third extraction stage to study the chemistry of the selected element. The wanted activity follows the green arrows, the black arrows represent feed and waste streams.

An alternative is to exploit gas phase properties of certain elements to suppress unwanted activity in the transport from the target chamber to the chemical apparatus. A good candidate for such separation is element 108, hassium. As has been shown in a recent GSI gas-phase experiments with hassium [11], it is possible to selectively transport Hs by oxidizing it to the tetroxide immediately after they escape the target chamber. Because the tetroxide is volatile, one does not need aerosol particles in the He gas-jet transporting the products to the chemistry apparatus. This reduces the background significantly in the detectors, because most of the unwanted activity will not be volatile and thus remains in the target chamber [12].

By dissolving the HsO_4 in a liquid phase in the SISAK degasser, it should be possible to study the liquid phase properties of Hs. Model experiments using ruthenium and osmium are planned and results will be reported at the TAN'03 conference.

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X-ray absorption fine structure spectroscopy of Zr and Hf in HCl solution for chemical characterization of Rf

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Introduction

Chemical behavior of the first transactinide element, rutherfordium (Rf), in hydrochloric acid solutions has been investigated by ion-exchange and solvent extraction methods together with the group-4 homologues Zr and Hf [1–5]. On the other hand, relativistic molecular density-functional calculations of electronic structure have been performed for hydrated, hydrolyzed, and chloride complexes of Rf, Zr, and Hf [6]. Although chloride complexation and hydrolysis of Rf have been considered in Refs. [1–6], no structural data of Zr and Hf in HCl solutions, which are essential to discuss the experimental results and to perform the theoretical calculations, are available. The Extended X-ray Absorption Fine Structure (EXAFS) measurements can provide information on the local environment around the central atom such as the atomic number and the number of neighboring atoms and their distance from the central atom. In the present work, we have measured EXAFS spectra of Zr complexes systematically in 1.0–11.5 M HCl. A change in the complex structure with HCl concentration is discussed together with our anion-exchange result of Zr [5].

Experimental procedures

Commercially available ZrCl_4 powder was dissolved with 1.0, 3.0, 5.0, 8.0, 9.0, 10.0, and 11.5 M HCl solutions to obtain 0.01 M concentration of Zr. EXAFS spectra were collected on the BL27B beam line using a Si (111) monochromator at the High Energy Accelerator Research Organization Photon Factory (KEK-PF). Measurements were performed in the fluorescence mode using a 7-element Ge detector at the Zr *K* edge. Curve-fitting amplitudes and phases were calculated by the FEFF8 code [7].

Results and discussion

Fourier transformed *K*-edge EXAFS spectra of the Zr complexes in 1.0, 3.0, 5.0, 8.0, 9.0, 10.0, and 11.5 M HCl solutions, which represent radial distribution functions of the atoms surrounding the Zr atom, are shown by solid curves in Fig. 1 together with the simulations by the FEFF8 code [7] by dotted curves. The FT peaks for shells Zr=O, Zr-O, Zr-Cl, and Zr---Zr are indicated by vertical dashed lines. The structural parameters, the number of neighboring atoms (*N*) and the distance to the neighboring atom (*R*) for shells Zr-O, Zr-Cl, Zr=O, Zr---Zr, and Zr---O, are summarized in Table 1. Accuracy of the *R* and *N* values was estimated to be about ± 0.02 Å and ± 0.5 , respectively. Note that the spectra shown in Fig. 1 are not corrected for the EXAFS phase shifts, ϕ , so that each FT peak position does not correspond to the real distance *R* in Table 1.

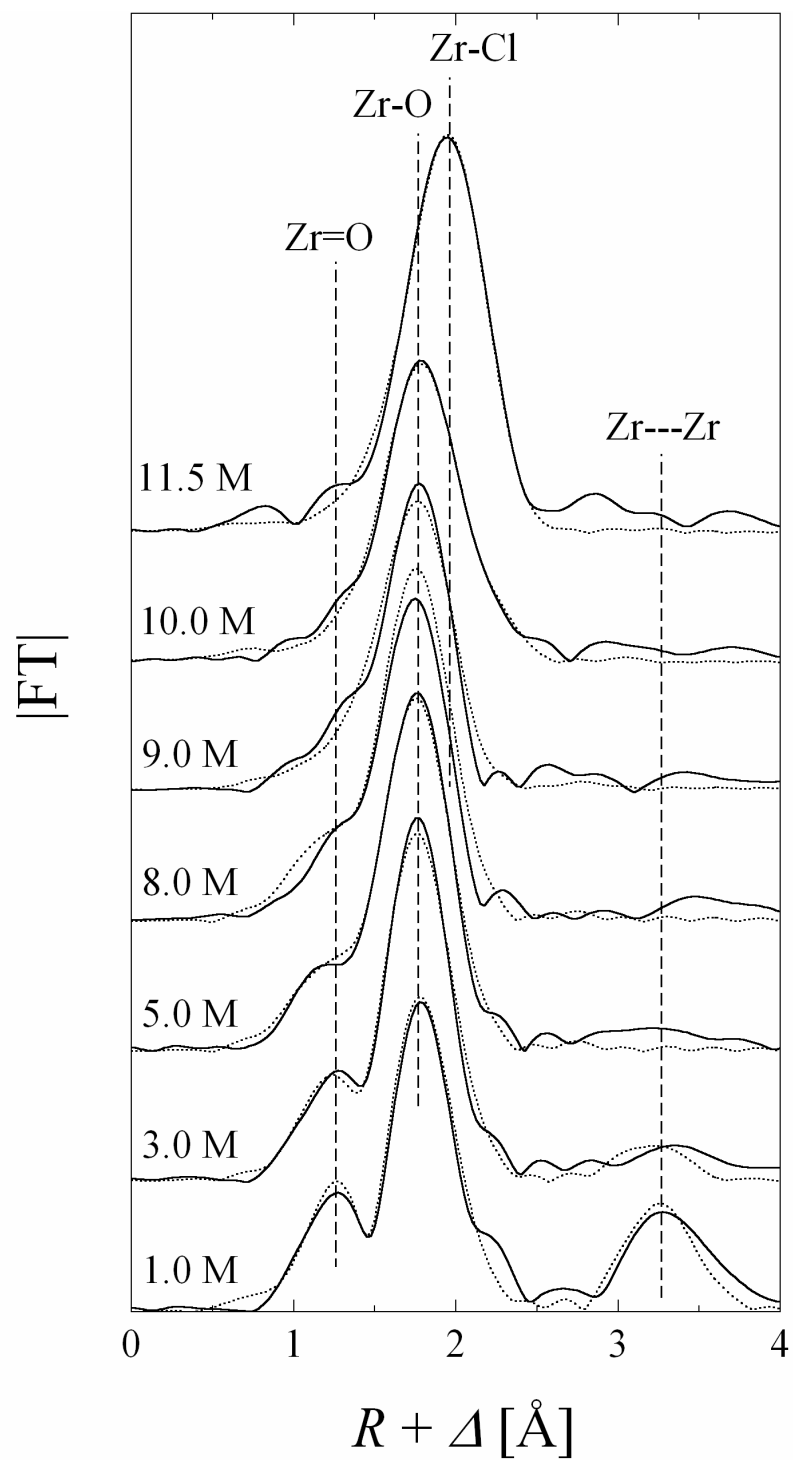


Figure 1. Fourier transformed K-edge EXAFS spectra of the Zr complexes in 1.0, 3.0, 5.0, 8.0, 9.0, 10.0, and 11.5 M HCl (solid curves) and the simulations by the FEFF8 code [7] (dotted curves).

Table 1. Structural parameters, the number of neighboring atoms (N) and the distance to the neighboring atom (R).

[HCl] (M)	Zr-O		Zr-Cl		Zr=O		Zr---Zr		Zr---O	
	N	R (Å)	N	R (Å)	N	R (Å)	N	R (Å)	N	R (Å)
1.0	6	2.21	-	-	1	1.63	1	3.58	4	4.95
3.0	6	2.20	-	-	0.5	1.63	0.5	3.58	-	-
5.0	6	2.21	-	-	0.8	1.65	-	-	-	-
8.0	6	2.22	-	-	-	-	-	-	-	-
9.0	7	2.23	-	-	-	-	-	-	-	-
10.0	4	2.21	3	2.43	-	-	-	-	-	-
11.5	-	-	6	2.43	-	-	-	-	-	-

In Fig. 1, the intense Zr-O peaks for Zr-OH₂ and/or Zr-OH⁻ bonds are seen at HCl concentrations of [HCl]=1–10 M. As listed in Table 1, the R values for the Zr-O shell are 2.20–2.23 Å and the N are 6–7. Above 10 M, the coordinated H₂O and/or OH⁻ are replaced with Cl⁻ with an increase of [HCl], and the Zr-Cl shell with $R=2.43$ Å appears. This change in the complex structure is reasonably consistent with that of the distribution coefficient (K_d) of Zr on the anion-exchange resin, CA08Y [5]. In the range of 1–7 M, the K_d values of Zr are almost constant, 2–4 mL g⁻¹, while at the higher [HCl], the K_d values increase steeply up to 10⁴ mL g⁻¹, forming the anionic hexachloride zirconium, ZrCl₆²⁻, at 11.5 M.

It is also interesting to note that the Zr=O peak with $R=1.63$ – 1.65 Å is shown in Fig. 1 at 1–5 M, though the Zr=O structure has not been reported in this system. Furthermore, the Zr---Zr peak, which indicates the formation of a dimer complex of Zr, is observed at the lower [HCl] of 1 and 3 M: presumably [(ZrO)(H₂O)₄]₂(OH)₂.

Previously, we investigated the anion-exchange behavior of Rf together with Zr and Hf in 4.0–11.5 M HCl [5]. It was found that the adsorption trend of Rf is very similar to that of Zr and Hf, indicating that Rf is typically the member of the group-4 elements. The adsorption order is Rf > Zr > Hf, which reflects a difference in the chloride complexing strength. Recently, we have conducted the EXAFS measurements for Hf in 1.0–11.5 M HCl. In the conference, the Hf result will be compared with that of Zr, and the chloride complexation and hydrolysis of Rf as well as Zr and Hf will be discussed by referring to the ion-exchange and solvent extraction results [1–5].

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First results of the CALLISTO-experiment: evidence for the formation of a hassate(VIII)

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Hassium, element 108, was produced in the fusion reaction $^{26}\text{Mg} + ^{248}\text{Cm}$ at the UNILAC accelerator of GSI [1]. A rotating target wheel with an average target thickness of $467\mu\text{g}/\text{cm}^2$ ^{248}Cm was used, partly together with a ^{152}Gd segment. After stopping in a He/O₂- mixture the recoils were oxidized, presumably to HsO₄, and were transported to the apparatus CALLISTO (Continuously Working Arrangement for Clusterless Transport of In-situ Produced Volatile Oxides), Fig.1. Nuclear reaction products could react with a NaOH surface under controlled humidity (2g H₂O/Kg gas); the nuclear decays of adsorbed species were detected with 16 PIPS-detectors (10x10mm² each), Fig. 2. In the detection array, a stainless steel plate, coated with 1 M ethanolic NaOH (on the average 20 μmol NaOH), is facing 4 detectors at a distance of 1mm. The volatile oxides are allowed to react with the thin alkaline layer, forming non-volatile products which are deposited. The deposition material was replaced every 60 minutes because the deposition efficiency decreases with time [1]. A possible explanation may be, that the alkaline surface is partially neutralized by CO₂, which is an impurity of the used gases and may be formed by a reaction of the carbon beam dump with the oxygen of the jet gas, too. Every 60 minutes, the 4 computer-controlled valves of the deposition and detection system switched one of the detector-arrays out of the gas flow. In this "service mode" the reactive surface can be renewed without interrupting the experiment. Thus a continuously measuring arrangement of 12 detectors was established. After 2 weeks of beam-time and an integral of 2.82×10^{18} beam particles, 5 correlated α -SF chains and one α - α - α -chain (Fig. 3,4) could be detected and attributed to the decay of Hs and / or Sg daughter. Due to pile-up from the high α -activity of Os, produced from the reaction $^{26}\text{Mg} + ^{152}\text{Gd}$ in the first part of the experiment, it was not possible to attribute 19 α - α -chains with appropriate energies and decay times to the decay of Hs; most of them were estimated to be random coincidences.

In analogy to OsO₄, HsO₄ presumably was deposited as Na₂[HsO₄(OH)₂], a hassate(VIII). A comparison of Hs to the Os-behavior (measured simultaneously) will be given.

References

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Figure 1. Diagram of CALLISTO.



Figure 2. Photograph of a detector array.

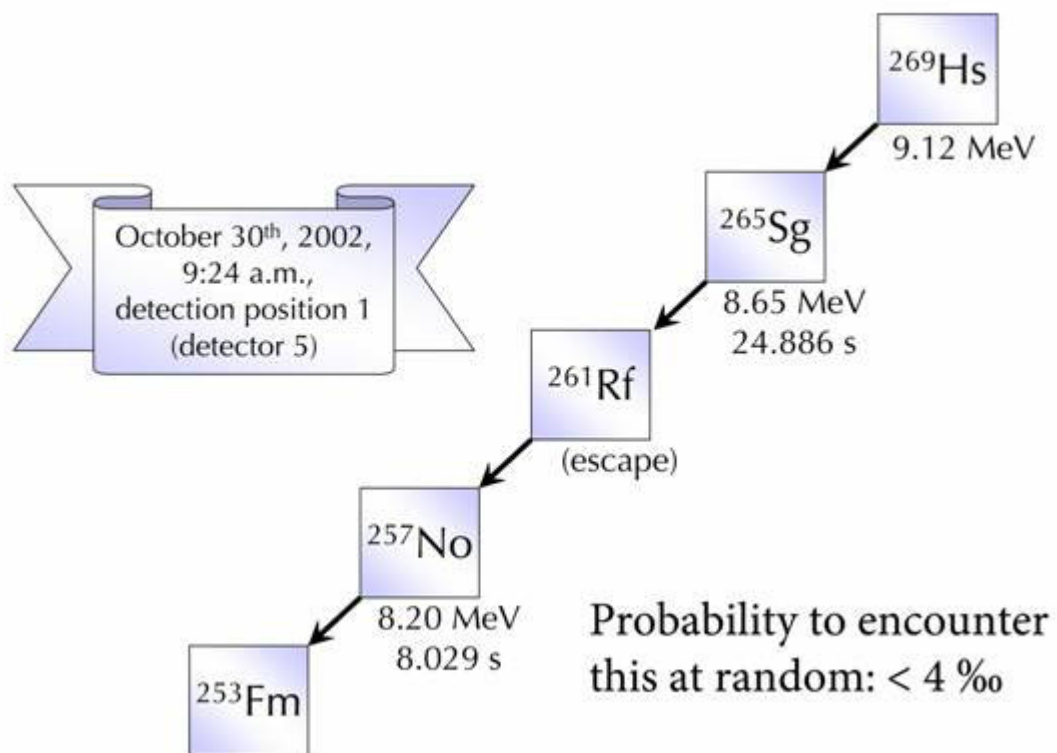


Figure 3. α - α - α -chain.

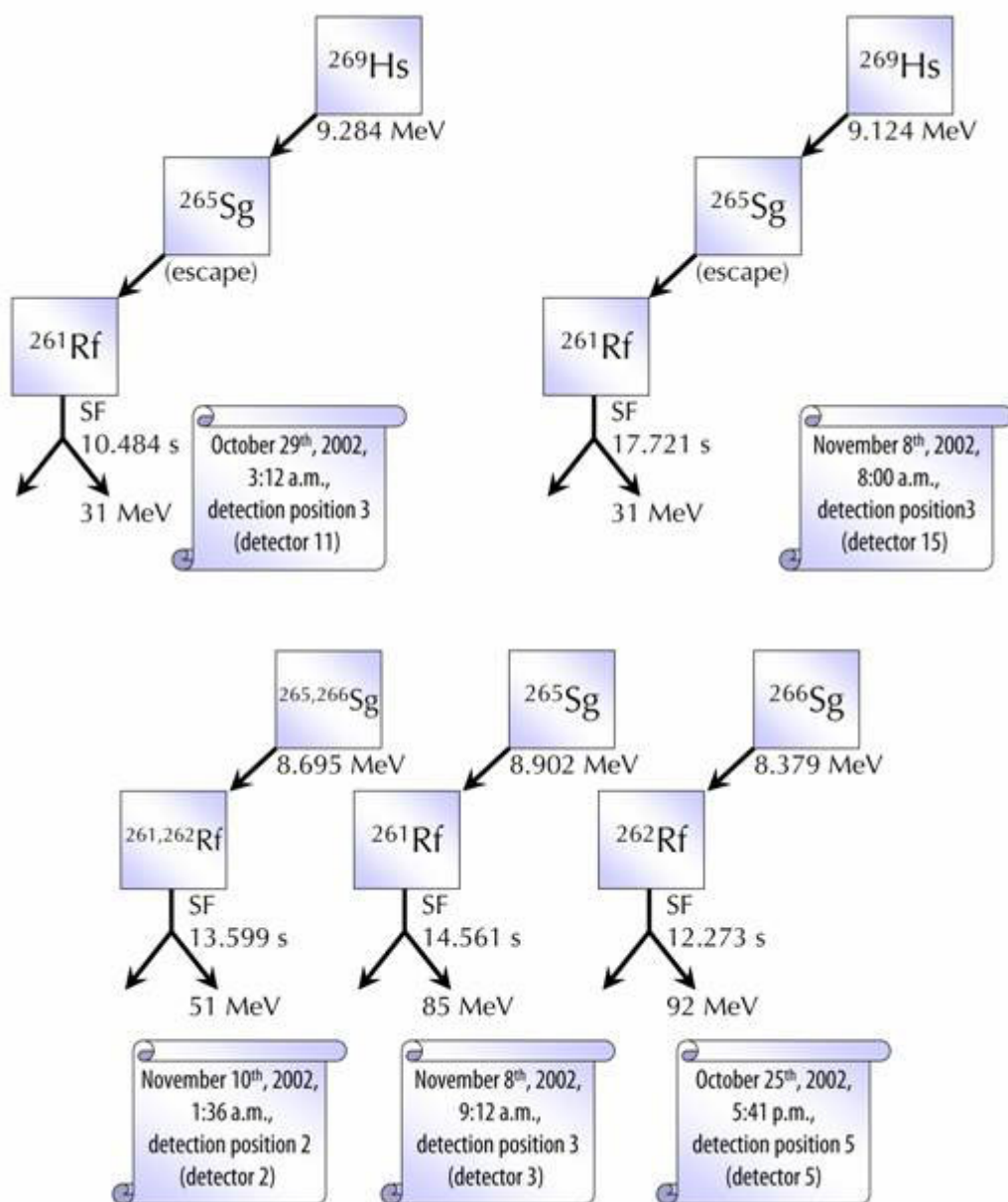


Figure 4. 5 α -SF –chains.

Gas phase studies of volatile group 4 metal complexes using the BGS - test experiments with Zr and Hf

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Introduction

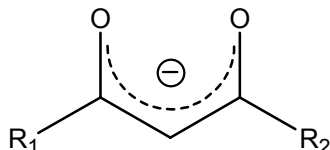
The chemical investigation of the transactinide elements (TAN, $Z \geq 104$), the heaviest elements known today, is an interesting topic of recent nuclear chemistry research. The strong electrical field of the highly charged nucleus accelerates the innermost electrons to relativistic velocities thus causing contraction of spherical (s, $p_{1/2}$) orbitals and expansion of the others ($p_{3/2}$, d, and f), which directly affects the chemical behavior of these elements. Deviations from trends established in the periodic table might therefore occur due to these so-called relativistic effects [1,2].

The heaviest elements which have been chemically investigated so far are the lighter TAN up to hassium (Hs, $Z=108$) [3,4] and element 112 [5,6,7]. More detailed studies have only been performed for the first two TAN, rutherfordium (Rf, $Z=104$) and dubnium (Db, $Z=105$). For Rf and Db, deviations from trends in chemical properties established by the lighter homologs have been observed in a few chemical systems [8,9], while for Sg, Bh and Hs such effects have not been reported so far. One important fact one has to bear in mind when assessing these results is the still rather scarce knowledge of the chemistry of elements heavier than Db which is mainly due to decreasing production cross sections and nuclear half-lives with increasing Z .

Gas chemical methods proved especially suitable to investigate TAN. Volatile inorganic compounds (e.g., halides or oxides) were investigated, and their adsorption behavior on different surfaces (usually quartz) was determined. For recent reviews see e.g., Refs. [10-12]. For several reasons, such as low production cross-sections, short half-lives, but also technical challenges, more sophisticated chemical studies have not been possible. One restriction in present TAN research is the plasma behind the target caused by the intense heavy ion beam. Any "weak" molecule (e.g., organic ligands) is immediately destroyed, thus limiting the possibilities of synthesizing chemical compounds directly behind the target to a few "simple" and robust inorganic compounds. It would be highly desirable to expand the knowledge on the chemical behavior of the TAN to classes of compounds that have not been investigated so far, e.g., volatile complexes or organometallic compounds. The use of a physical pre-separator, e.g., the Berkeley Gas-filled Separator (BGS) [13,14] allows separating the beam from the desired TAN isotopes, thus making such studies possible. The BGS is currently the only device worldwide that is used as a pre-separator for chemistry experiments and its power was recently demonstrated in liquid-liquid extraction experiments with Rf [15] but also in extraction studies with short-lived isotopes of lighter homologs [16]. With the beam separated in the BGS, less robust molecules can be introduced directly into the gas volume where nuclei recoiling from the BGS are thermalized. Therefore, it appears possible to form volatile organometallic compounds or metal complexes of TAN in-situ in the so called recoil-transfer-chamber (RTC) [17]. These species can then be rapidly transported to a chromatography setup and detection system.

Volatile β -diketonate metal complexes

A compound class that appears suitable for such studies are the β -diketonates, i.e., coordination compounds of a metal with ligands of the general structure shown below:



The β -diketonate anions are well known to act as bidentate ligands forming neutral complexes some of which can be transferred to the gas phase without decomposition. It has been experimentally observed that the introduction of fluorine (F) atoms to the system significantly enhances the volatility [18,19]. Therefore the trend in volatility (or sublimation enthalpy, ΔH_{sub}) for 2,4-pentanedionates (acetylacetonates, acac; $R_1=R_2=\text{CH}_3$), 1,1,1-trifluoro-2,4-pentanedionates (1,1,1-trifluoroacetylacetonates, tfa; $R_1=\text{CF}_3$; $R_2=\text{CH}_3$) and 1,1,1,5,5,5-hexafluoro-2,4-pentanedionates (1,1,1,5,5,5-hexafluoroacetylacetonates, hfa; $R_1=R_2=\text{CF}_3$) is generally given as:

$$\Delta H_{\text{sub}}[\text{M}(\text{acac})_n] > \Delta H_{\text{sub}}[\text{M}(\text{tfa})_n] > \Delta H_{\text{sub}}[\text{M}(\text{hfa})_n].$$

Recently, Ono et al. studied the behavior of ^{252}Cf fission products that were combined with another β -diketone anion, 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane dpm; $R_1=R_2=\text{C}(\text{CH}_3)_3$) in isothermal gas chromatography experiments and observed the selective formation of volatile Ru and Rh compounds [20]. Greulich and co-workers reported on the successful separation of nine lanthanide elements and yttrium in the form of hfa complexes using gas chromatography [21]. The fractional sublimation of ^{86}Zr and $^{87\text{m}}\text{Y}$ as fluorinated β -diketonate complexes as an example of the separation of radioisotopes is also reported [19]. In studies of β -diketonates of Sc, Yb, and Hf using carrier-free isotopes produced simultaneously in heavy-ion induced fusion reactions, Fedoseev and coworkers demonstrated that single molecules of Hf-hfa complexes deposited at temperatures below 100°C in a temperature gradient tube [22]. However, no separation of the three elements could be achieved. This may also be the case for different nuclides formed in nuclear reactions. However, by employing a physical pre-separator this should no longer be a problem, since transfer products are strongly suppressed by the BGS. We therefore envisaged to use the hfa system for first studies of a volatile metal complex.

Experimental / Results

Our studies are directed towards an experiment with the lightest TAN, Rf, since ^{257}Rf ($T_{1/2}=4.7$ s) can be produced at a relatively high rate of 1-2 atoms/s at the BGS [15]. A natural first step towards an experiment with a transactinide is the investigation of its lighter homologs, i.e., Zr and Hf for group 4.

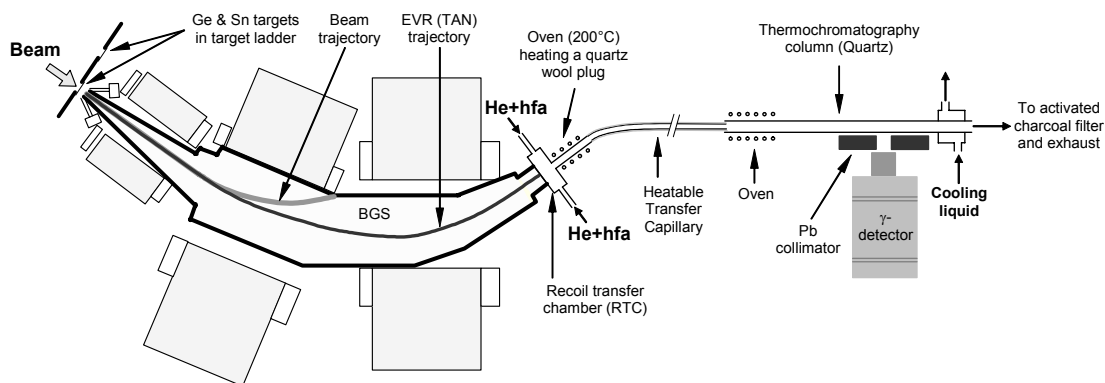
Production of short-lived Zr and Hf isotopes using a heavy ion cocktail

To rule out the role of differing experimental conditions in the measurement of chemical properties, it is desirable to investigate isotopes of several homologs simultaneously. Due to their different magnetic rigidities, BGS cannot forward them to the chemistry setup simultaneously. The next best approach is to switch quickly between short-lived isotopes of these elements without having to open the chemistry setup. This can be achieved when they can be produced in heavy-ion induced fusion reactions employing

beams of similar A/q and E/A which can be generated simultaneously in the cyclotron. This technique is referred to as a heavy-ion cocktail and already employed at the 88 inch cyclotron [23]. In first experiments, short-lived Zr and Hf isotopes were produced by using a cocktail of $^{18}\text{O}^{4+}$ and $^{50}\text{Ti}^{11+}$ with $E/A \sim 4.5$ MeV/n and their magnetic rigidities ($B\rho$) in dilute He were measured. Three different Sn targets ($^{116,120,124}\text{Sn}$) and a $^{\text{nat}}\text{Ge}$ target were mounted on a target ladder installed at the irradiation position of the BGS allowing for quick switching from Zr to Hf production.

Formation and observation of volatile hfa compounds of Hf

A schematic of the experimental setup is shown in the following Figure:



The beam delivered by the 88 inch cyclotron induces nuclear reactions in the target at the irradiation position. The beam is deflected using the BGS and does not reach its exit. The evaporation residues (EVR) enter the RTC through a thin Mylar window and are thermalized in the RTC. hfa-enriched He is introduced into the RTC and it transports the EVRs to a nearby oven kept at an elevated temperature. In first experiments, the formation of a volatile compound of Hf was observed when hfa was present in the carrier gas, while no Hf was transported out of the RTC in a pure He gas flow. In irradiations of $^{120,124}\text{Sn}$ with ^{50}Ti , ^{165}Hf ($T_{1/2}$: 76 s) and $^{168-170}\text{Hf}$, respectively, were observed in an activated charcoal catcher mounted at the exit of the RTC.

Outlook

The next on-line experiments will aim at a thermochromatographic (TC) [24] investigation of the formed compounds. Since hfa complexes are known to be relatively stable [18,19], it should be possible to transport them through a capillary kept at an elevated temperature to an on-line TC apparatus. This apparatus consists of an open quartz column along which a longitudinal negative temperature gradient is established. The distribution of the radionuclides along the gradient will be measured with a γ -detector. Using a lead collimator allows for achieving a spatial resolution of one centimeter. These experiments are under way. Parallel to the on-line studies, complementary experiments with macroamounts of Zr and Hf as well as off-line TC studies using long-lived radionuclides are being performed. First results will be reported at the conference.

Conclusion

With the planned synthesis of a new class of compounds of TAN, namely volatile coordination complexes, a more thorough investigation of their chemical properties becomes possible. These results

are complementary to those gained in past gas chemical studies as well as those in aqueous phase and will help elucidating the influence of relativistic effects in the chemistry of the heaviest elements. The validity of the periodic table in the region of the heaviest elements is still a fundamental question that cannot be fully answered at the moment, and predictions concerning even heavier elements are controversial. Future studies could then also include heavier TAN since the basic experimental system appears to be relatively easily adaptable to other similar chemical systems.

Acknowledgments

Fruitful discussions with W.W. Lukens are gratefully acknowledged. We thank the staff of the 88-inch cyclotron and the ion source team for the production of the O/Ti-cocktail beam. This work was supported by the Swiss National Science Foundation and the Office of Science, Office of High Energy and Nuclear Physics, of the U.S. Department of Energy.

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Simultaneous measurement of volatility of Zr, Hf and Rf

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Rutherfordium belongs to the group-4 elements as Zr and Hf. It is well known that the chemical properties of Zr and Hf very resemble with each other and halides of these elements are volatile. From the relativistic calculations RfCl₄ is predicted to be more volatile than ZrCl₄ or HfCl₄ [1-3], whereas from the extrapolation, exactly the opposite trend is expected [4,5]. In this special case, the predictions about the relative volatility of RfCl₄ compared to ZrCl₄ and HfCl₄ can be directly tested experimentally in a gas phase.

Türler et al. investigated the volatility of the Hf- and Rf- chlorides with OLGA II [6,7]. They showed that the volatility of the chlorides of the group-4 is very similar among them. Later, HEVI system was developed by Kadkhodayan *et al.* [8] and the volatility of the Zr, Hf and Rf chlorides was investigated. The result shows that the order of volatility is RfCl₄ > ZrCl₄ > HfCl₄ [9]. However, each chloride was studied in a separate experiment, so that chemical conditions may have been different among the experiments. And the reported correlation is not consistent that expected from the sublimation enthalpies of Zr and Hf. Türler *et al.* [10] investigated the volatility of the Hf- and Rf- chlorides again, and they showed RfCl₄ > HfCl₄ in volatility but did not discuss about Zr chloride.

In the present work, in order to clarify the above mentioned ambiguity, the investigation for volatility of Zr, Hf and Rf chlorides was performed under the identical conditions.

The isothermal chromatographic apparatus consists of a reaction chamber, an isothermal column, and a re-clustering chamber. Each section is made by quartz and connected in a series. The isothermal column is a spiral tube with the 2000 mm long and 3 mm inner diameter. The reaction chamber and the isothermal column were heated independently up to a maximum temperature of 1200° C by electric furnaces.

In order to investigate the isothermal gas chromatographic behavior of Zr, Hf and Rf in the same condition, an irradiation for the production of Zr, Hf and Rf isotopes were performed at the same time at the JAERI 20-MV Tandem accelerator. A target chamber and an irradiation setup are shown in Fig. 1. ⁸⁵Zr was produced by the ^{nat}Ge(¹⁸O, xn) reaction. ^{167,169}Hf were produced by the ¹⁵²enriched Gd(¹⁸O, xn) reaction and ²⁶¹Rf was produced by the ²⁴⁸Cm(¹⁸O, 5n) reaction.

Produced activity is transported from the target chamber to the gas chemistry apparatus via He/KCl gas-jet transport system. The activity-laden aerosols were transported by the helium through a 2.2 mm i.d. stainless steel tube to the gas chromatography apparatus. The stainless steel capillary was employed in order to eliminate any exchange of oxygen through the capillary walls. The concentration of residual oxygen was monitored with the oxygen monitor and was less than 30 ppm for experiment. Domanov *et al.* observed that in gas chromatography experiments the transportation of Zr and Hf chlorides could not be affected by oxygen in this order of amounts [11]. As a chlorinating agent, a mixture of chlorine gas and carbon tetrachloride vapor was used. Chemical reaction took place in the reaction room at 1000° C. The chemically separated species were attached to new KCl aerosol, and transported for α measurement to the detection system MANON [12], which is a rotating wheel detection system with a 80 cm ϕ wheel, 80 collection positions, and six pairs of Si PIN photodiodes. The activity-laden aerosols were deposited on a

polyethylene terephthalate foil of $120 \mu\text{g}/\text{cm}^2$ in thickness and 20 mm in diameter. Each sample was collected for 30 s and measured for 180 s.

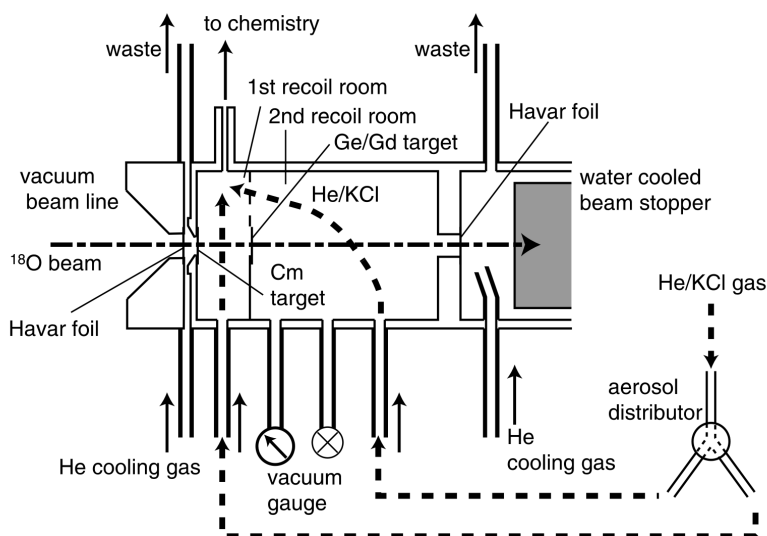


Figure 1. Schematic of the target chamber utilized for simultaneous production of Zr, Hf and Rf isotopes.

The obtained α spectrum is depicted in Fig. 2. The spectrum is dominated by α -lines from the contaminants ^{211}Bi and $^{211\text{m},212\text{m}}\text{Po}$ which also form volatile chlorides. Due to the much effort to prevent Pb contamination, the level of background α -particles from them was reduced compared with those by Kadkhodayan *et al* [9]. The α -particle group of 8.00-8.40 MeV was assigned to ^{261}Rf ($T_{1/2}=78$ s) and its daughter ^{257}No ($T_{1/2}=26$ s).

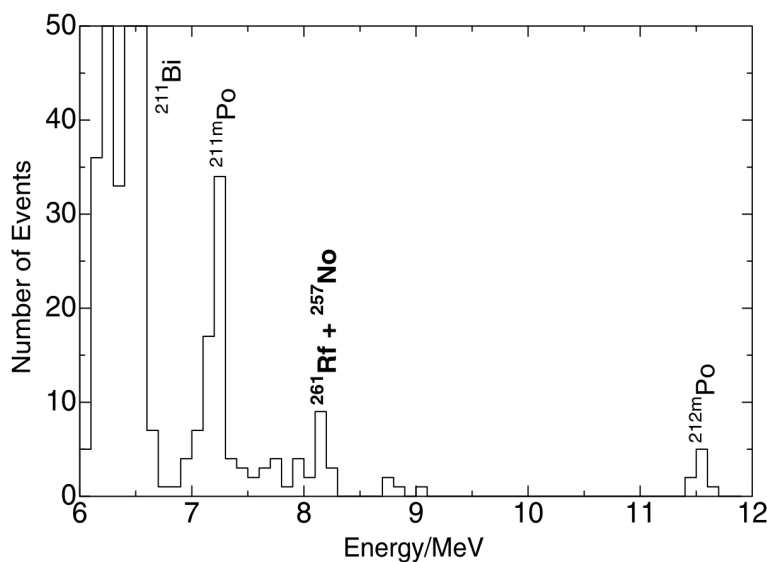


Figure 2. α spectrum after chemical separation.

In Fig. 3 the measured yields of the 8.00-8.50 MeV α -particle group, that of the 454 keV (^{85}Zr) and of 493 keV (^{169}Hf) are shown as a function of the temperature of the isothermal column. At the isothermal temperature of 300° C, a part of Zr, Hf and Rf chlorides were transported to the outlet of the isothermal column. The yield of Zr, Hf and Rf chlorides increased rapidly with the increase of the isothermal temperature, and reached the maximum around 350° C. This rapid change of yield with column temperature is characteristic of the simple adsorption-desorption transport mechanism [13]. Furthermore, since oxygen concentration was kept at less than 30 ppm in the system, it was not considered that the oxychlorides would be concerned with chromatographic transportation [11]. Therefore, it was concluded that the volatile compounds of these three elements would be the tetrachlorides and that they would behave very similar to each other.

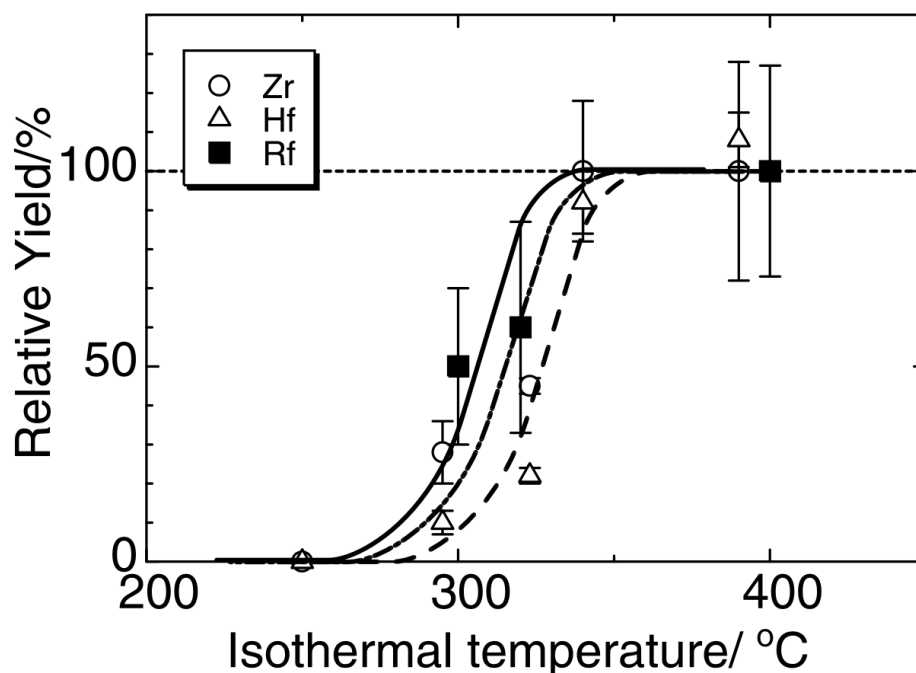


Figure 3. Relative yield curves for ^{85}Zr -, ^{167}Hf - and ^{261}Rf -chlorides. The lines are calculated yield curves from a Monte Carlo simulation.

It should be mentioned that after prolonged gas chemistry experiments in the present work, the quartz surface of the chromatography column is partially coated with a thin layer of KCl, which means that of the chromatography was performed on KCl rather than on SiO_2 . As a volatility measurement is strongly dependent on the column surface, we cannot directly compare the present results to those of others. However, relative comparison among the elements is supposed to be reasonable. In this work, Zr and Hf were examined simultaneously, and it was found that the volatility of their chlorides was similar with each other. This result agrees with the expectations from macro scale chemistry. Since Rf chlorides behaved similarly with Zr and Hf on this surface, it is expected that Rf chlorides would have similar volatility. An adsorption enthalpy was calculated using a Monte Carlo simulation based on a microscopic model [14-16] and the following adsorption enthalpies for the group-4 chlorides were obtained for partially KCl coated quartz surfaces: Zr: -118 ± 6 kJ/mol, Hf: -116 ± 6 kJ/mol and Rf: -112 ± 10 kJ/mol. ZrCl_4 and HfCl_4 were found to have very similar adsorption enthalpies. This tendency is consistent with the results for NaCl surface [17,18].

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Electrochemistry at the tracer scale - an approach to aqueous superheavy element chemistry

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Due to the recent successful gas-phase experiments with hassium [1, 2] and element 112 [3] the focus of aqueous heavy element chemistry shifted also in that region of the periodic table. Theoretical predictions by Fricke et al. [4] suggest, that the superheavy elements 112-118 have a noble metal character. These predicted properties led to an electrochemical approach for first aqueous studies of the superheavy elements. The electrochemical deposition of tracer amounts on a metal surface usually does not lead to a complete coverage of the electrode. Such sub-monolayer electrodepositions cannot be described by the Nernst equation and may take place at more negative (overpotential deposition, opd) or at more positive potentials (underpotential deposition, upd), depending on the properties of tracer and electrode material. Using macroscopic thermodynamic models, Eichler et al. proposed a modified Nernst equation to describe the electrodeposition of tracer amounts on a given electrode material [5]. They calculated potentials for the deposition of 50% of the tracer ion on a foreign electrode material. In an earlier work, $E_{50\%}$ -values of the elements 112-116 were predicted on the basis of relativistic Dirac-Slater calculations [6]. Pd- and Pt-systems have the highest $E_{50\%}$ -values and should be preferable electrode materials for electrodeposition experiments. To design an electrochemical deposition experiment for super-heavy elements, we have to investigate how the predicted $E_{50\%}$ -values correspond to experimental upd-potentials for the homologs of the elements 112-116 and if a spontaneous deposition of the tracer is possible. Furthermore, we have to figure out what kind of electrode pretreatment is necessary to achieve a clean surface and - due to the very short half-lives of the superheavy isotopes - how a quantitative electrochemical deposition can be performed in a very short period of time. In the first batch experiments with the lighter homologs of the superheavies, we kept our focus on lead (homolog of 114) and polonium (homolog of 116) because carrier free trace amounts of those elements were easy to obtain. ^{212}Pb was obtained via electrostatic gas phase collection of the decay products from a ^{220}Rn emanating source (^{228}Th co-precipitated with Zr-Stearate), whereas ^{210}Po was extracted from irradiated bismuth by ion-exchange chromatography. Already the first experiments, especially with lead, showed, that the spontaneous electrodeposition is a relatively slow, diffusion controlled process. Therefore, we continued the work on two different paths. The lead experiments were now performed under a controlled potential using standard electrochemistry equipment. The polonium studies, on the other hand, continued to look into the involved parameters for the spontaneous deposition. Reproducible results in electrochemical experiments can only be achieved by using electrodes with very clean surfaces. To get such electrodes, a first procedure was established, where the electrodes (metal foils) are cleaned by heating under an argon/hydrogen (95:5) atmosphere at about 700K to remove oxides from the surface. Using a 0.1M HCl solution of ^{210}Po , a series of experiments on the spontaneous electrodeposition of Po has been performed. During these studies a range of parameters was varied. The experiments used Cu, Ag and Ni in form of 6x6mm foils as electrode materials. These foils were introduced into a small electrochemical cell with a volume of only 200 μl [7]. To get information about the influence of the solvent and its dielectric properties on the deposition process, mixtures of ^{210}Po in 0.1M HCl with organic solvents (acetone, dioxane) were used. To assure a maximum ion motion towards the electrode, the cell was heated to 340K and treated with ultrasound. In these experiments, relatively long reaction times of 5min and 1min were chosen. The determination of the amount of deposited Po was performed by α -spectroscopy.

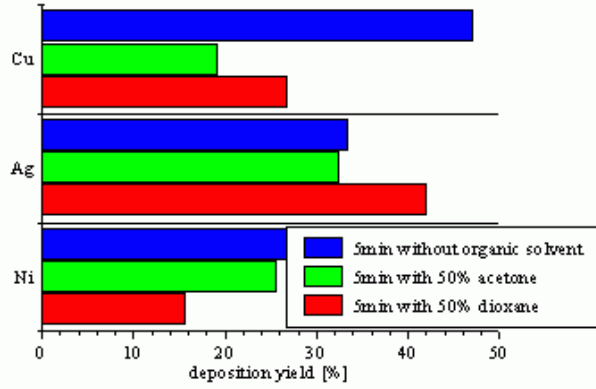


Fig.1: Deposition yields of Po-210 from 0.1M HCl on Cu, Ag and Ni

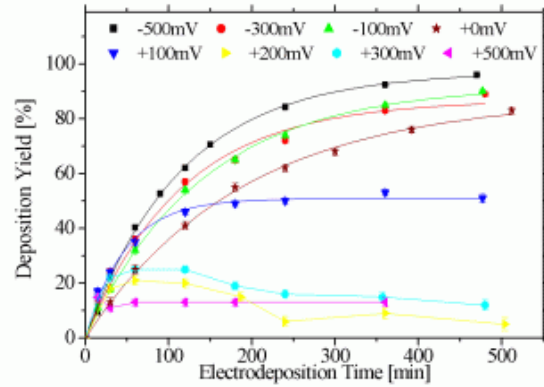


Fig.2: Electrodeposition of Pb on a Pt-electrode in 0.1M HCl vs. time at different potentials

The measured deposition yields (figure) did not show any clear trend with respect to the variation of the reaction time and the change in solvent characteristics. This result can only be attributed to variations in the properties of the electrode surface. Thus, the used cleaning process might still be not sufficient to get reproducible results. As an alternative cleaning process, an electrochemical treatment will be used, where the electrode is cleaned by a quick electrolysis process. After that, it will be stored in a solution of the electrolyte used in the later experiments. This process should prevent the surface from being exposed to air and therefore from being contaminated with oxygen and aerosol particles. Hevesy and Paneth defined the "critical potential" E_{crit} as the potential, at which electrodeposition of a radiotracer on a metal electrode first occurs [8]. Obviously, measured E_{crit} -values should be similar to the predicted $E_{50\%}$ -values. To determine the critical potential of the Pb-upd on Pt electrodes, we used a potentiostatic three-electrode-system with a Ag/AgCl (3M KCl) reference electrode, a Pt working electrode, and a Pt counter electrode. The area of the working electrode was 2cm², the total volume of the 0,1M HCl electrolyte solution was 20ml. For agitation, we applied a constant nitrogen flow. Prior to the experiment, the working electrode was electrochemically cleaned. To determine the deposition yield of ²¹²Pb vs. the electrodeposition time without disturbing the system, we measured the decrease of the activity in the solution by γ -spectrometry. The experiment was repeated at different electrode potentials. According to Joliot [9], the electrodeposition rate of a radiotracer is described by

$$dN_{dep}/dt = DF_E/\delta V \cdot (kN_{tot} - N_{dep}). \quad (1)$$

After integration, a relation between the deposition yield N_{dep}/N_{tot} and the reaction time is obtained

$$N_{dep}/N_{tot} = k - k \cdot \exp(-DF_E/\delta V). \quad (2)$$

Here, N_{dep} is the amount of atoms deposited, N_{tot} is the total amount, D is the diffusion coefficient, F_E is the electrode surface, δ is the Nernst diffusion layer and V the volume of the solution. The term k represents the maximum deposition yield that can be reached for the given potential E . In the experiment, we obtain a relation between the deposition yield and the electrodeposition time (Fig.2). After fitting with equation 2, we get the maximum deposition yield k for each potential E (Fig.3). The critical potential E_{crit} for the deposition of Pb on Pt from 0.1M HCl is about +190mV. This value corresponds roughly to the critical potential of +255mV for the deposition of Pb on Pt in 1N HNO₃ measured by Ziv et al. [10]. The predicted $E_{50\%}$ -value of +10mV [5] is somewhat lower than the measured E_{crit} -value, but the difference gets smaller if compared with the potential at which the maximum deposition yield is 50% (approx. +100mV).

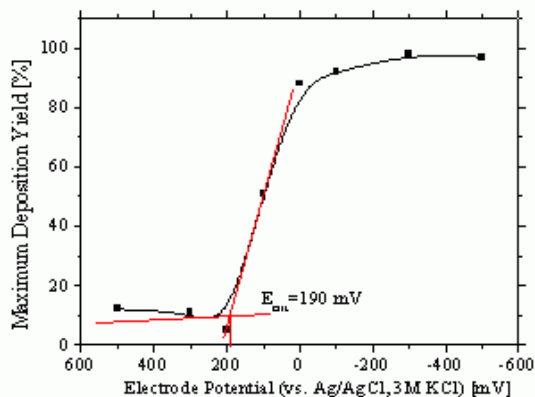


Fig.3: E_{on} for the Pb-upd on Pt-electrodes in 0.1M HCl

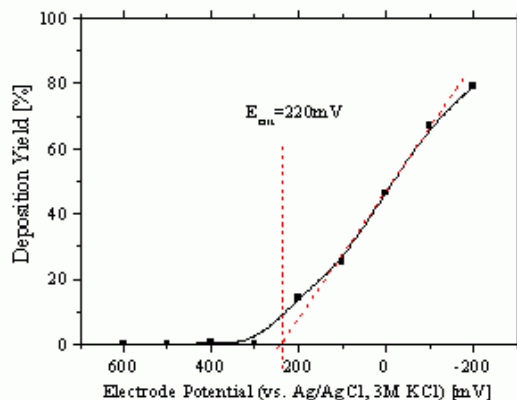


Fig.4: E_{on} for the Pb-upd on Pd-electrodes in 0.1M HClO₄

According to equation (1), the electrodeposition rate dN_{dep}/dt increases with E/V . As a consequence, we reduced the dimensions of the electrolytic cell to a total volume of 150 μ l and an electrode surface of 0.36 cm². The deposition rate also depends on the thickness of the Nernst diffusion layer. To keep it low, we agitated the solution with a magnetic stirrer. As reference electrode, we used a micro-Ag/AgCl-electrode. In this experiment, we used Pd as electrode material, and the electrolyte was 0.1M HClO₄. Compared to the "macro-experiment" described above, the electrodeposition rate increased - as calculated - by a factor of 24. After 10 minutes, the deposition yield is near to its maximum possible value. After the deposition, the electrode was removed while under current, washed with water and measured on a γ -detector. No activity was lost during the washing process. Fig.4 shows, that no activity is deposited until the critical potential of about +220 mV is reached. From this point on the deposition yield increases with the applied potential. The critical potential we determined in the Pb/Pd-system is similar to that in the Pb/Pt - system. However, a remarkable difference between the two systems is, that the deposited activity can be easily removed from Pt-electrodes by mineral acids, but not from Pd-electrodes. In future experiments, we will further improve the electrolytic cell dimension to obtain reaction times in the range of seconds. For online experiments at the Mainz TRIGA reactor and at GSI, an automated apparatus using a tape technique to provide the electrode material is planned. This device will combine the electrode cleaning step, the electrochemistry step, and the detection system.

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Ion exchange and extraction chromatographic studies with homologs of seaborgium (element 106) in HNO₃-HF medium

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The experiments to understand the chemical behaviour of transactinides such as Rutherfordium (Element 104) and Seaborgium (Element 106) are of considerable interest from basic chemistry point of view. ²⁶¹Rf and ²⁶⁵Sg have been produced by heavy ion reactions using intense beams of O-18 and Ne-22 on ²⁴⁸Cm target, respectively [1]. Due to their short half lives ($t_{1/2}$ of ²⁶¹Rf and ²⁶⁵Sg are about 78 s and 34 s, respectively) and limited availability of accelerator beam time for such exotic experiments, it is relevant to develop separation methods using their homologs such as Zr, Hf, (for Rf), Mo and W (for Sg) and pseudo-homologs viz. Th (for Rf) and U (for Sg) for utilization as a guide line for the actual experiment.

Rapid radiochemical separation methods involving Multi-Column Technique (MCT) have been used for the studies on the chemical properties of trans-actinides involving experiments in HNO₃ + HF medium using anion exchangers such as DOWEX 1x8. However, the K_d values of homologs like Mo and W were found to be too high when DOWEX 1x8 resin was used suggesting the need for weaker anion exchangers. The present work is an attempt in that direction where several other anion exchangers with different functional groups have been used along with an extraction chromatographic material made from Aliquat 336, a liquid anion exchanger, in chloroform.

As reported earlier, the contrasting K_d values obtained at 0.01 M HF and 0.1 M HNO₃ are made use of in a proposed scheme for the studies on the chemistry of Sg [2]. Table 1 lists the K_d values for Mo and W with three different anion exchange resins viz. DOWEX 1x8 (with – methyl group), HS 36 (with – ethyl group) and HB 36-I/92 (with – n-butyl group). The batch distribution data are obtained in the 0.1 M nitric acid as well as HCl in the presence of 0.01 M HF. As shown in the following table, the K_d values are significantly larger for the HCl medium as compared to the HNO₃ medium. This can be ascribed to two reasons, first, the chloro complexes are more easily formed than nitrate complex and second, the nitrate ion acts as a better counter anion. As shown in Table 1, the K_d values at 0.1M HNO₃ + 0.01M HF show a decreasing trend of Dowex 1x8 > HS 36 > HB 36-I/92 for Mo, while an opposite trend is observed for W. On the other hand, at 0.1M HCl + 0.01M HF, the trend for both Mo and W is Dowex 1x8 > HS 36 < HB 36-I/92. The results of the ARCA experiments carried out on-line with the accelerator produced ¹⁷⁰W have indicated reasonable agreement with those from the batch studies mentioned above.

Table 1. Effect of resin type on the K_d values of Mo and W

Conditions	Mo			W		
	DOWEX 1x8	HS 36	HB 36-I/92	DOWEX 1x8	HS 36	HB 36-I/92
0.1M HNO ₃ + 0.01M HF	89	15	5.7	5.0	13	16
0.1M HCl + 0.01M HF	181	40	732	96	46	70

In spite of using three different functionalized ion-exchangers, it was not possible to obtain an experimental condition for which the K_d values of Mo and W fall in the range of 10-50. An extraction chromatographic material was prepared using Aliquat 336 (tri-caproyl methyl ammonium chloride) in chloroform sorbed onto chromosorb W. Figure 1 shows the results obtained with the extraction chromatographic studies carried out at varying concentration of HF at a fixed concentration (0.1M) of nitric acid using Mo and W tracers. It is interesting to note that the sorption of Mo and W onto the extraction chromatographic resin material is significantly high at lower HF concentration. It is attributed to the presence of anionic oxo complexes like MoO_4^{2-} and WO_4^{2-} . The decrease in the K_d values with increasing HF concentration in the case of Mo and W could be explained on the basis of the formation of neutral complexes such as MoO_2F_2 and WO_2F_2 . On further increasing the HF concentration, the K_d values of W showed an upward trend while no such trend was seen with Mo. This is explained on the basis that though both the hexavalent Mo and W form anionic fluoride complexes, it is more favorably and readily formed for the latter [2]. The V-shape curve for W was observed earlier when DOWEX 1x8 was used as the ion exchanger [3]. The interesting aspect observed during these studies was that the K_d values are such that (Mo: 45 and W : 18 at the aqueous phase composition of 0.1M HNO_3 + 0.01M HF) experiments with ^{265}Sg can be carried out conveniently. These are much lower than the values obtained with DOWEX 1x8 suggesting that the Aliquat 336 loaded chromatographic material can be an ideal choice for the chemical studies involving ^{265}Sg .

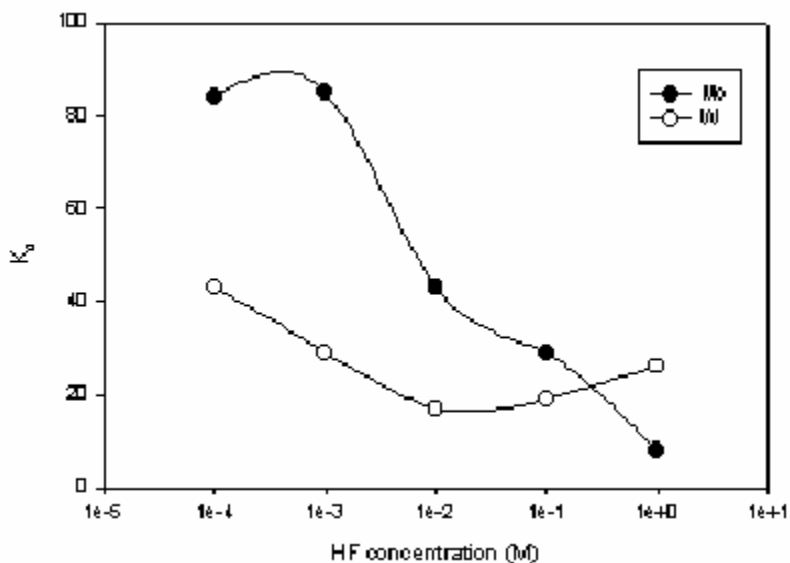


Figure 1. Distribution of Mo and W as a function of HF concentration at 0.1 M HNO_3 . Resin: Aliquat 336 sorbed on chromosorb.

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A liquid-liquid extraction system suitable for studying the chemistry of rutherfordium with SISAK

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Introduction

A general presentation of the on-line liquid-liquid extraction system SISAK is given in another presentation to the TAN'03 conference (J.P. Omtvedt and coworkers). The presentation given here describes a system suitable for the investigation of the chemistry of rutherfordium. This work is in progress, and *the results presented are preliminary*.

In 2000 and 2001 a pilot SISAK chemistry-experiment with the transactinide rutherfordium was performed at the Lawrence Berkeley National Laboratory (LBNL) in Berkeley, USA. In this experiment it was proved that it was possible to extract and detect the ~4 s transactinide ²⁵⁷Rf with SISAK [1].

The ²⁵⁷Rf activity was produced with a 235 MeV ⁵⁰Ti¹²⁺ beam from the LBNL 88-inch cyclotron hitting a rotating ²⁰⁸Pb target. The recoils from the target were separated in the Berkeley Gas-filled Separator (BGS). After this, the recoils were transferred from the BGS focal plane into a gas jet by using a then newly constructed Recoil Transfer Chamber (RTC). The activity is transported to the SISAK system with a gas jet. First, in the degasser step, the activity is transferred from gas phase to an aqueous phase, then the activity is extracted with a suitable extraction agent into the organic phase. By carefully selecting the conditions and extraction agents, properties like valence state, charge state, the number and type of ligands can be investigated. The extracted rutherfordium (in the organic phase) is then mixed with a scintillator cocktail and pumped through Liquid Scintillation (LS) detectors. The amount of rutherfordium remaining in the aqueous state can currently not be measured, but must be calculated from measurements of how much activity is entering the SISAK system. An overview of the complete setup is shown in Fig. 1.

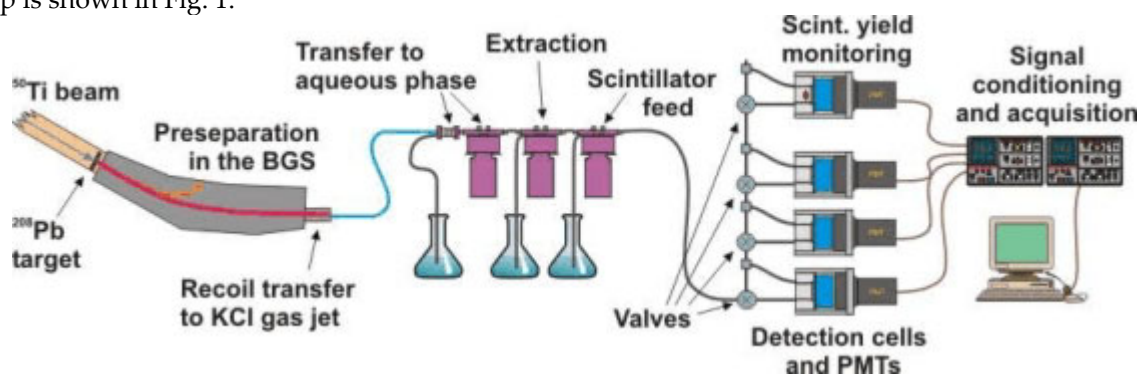


Figure 1. Overview of the complete SISAK setup for transactinide experiments.

As reported in one of our other TAN'03 contributions (J.P. Omtvedt and coworkers), the chemistry system (extraction with dibutyl-phosphate from nitric acid) used in the 2000 and 2001 experiments was not found suitable for detailed chemistry studies of Rf. Therefore the still on-going work reported here was initiated to find a suitable system for investigation of the liquid-phase chemistry of Rf with SISAK.

Search for a suitable extraction systems for Rf experiments

A chemical system, i.e. the concentration and flow rates of the reagents, and the solvents used, must meet a number of criteria to be suitable for a SISAK type of chemical investigation of transactinides:

1. Good separation of Zr and Hf. This is because it is of interest to be able to classify the behaviour of rutherfordium as either Zr or Hf like.
2. No adverse effects (like adsorption) between the chemicals used and the construction material of the SISAK equipment.
3. The complexation and extraction rates must be fast. The contact time between the two liquid phases is between 0.5 and 0.1 s. Therefore the reaction rate must be fast enough to at least approach equilibrium.
4. No (or only small) interference with the liquid scintillation used to detect the α activity can be allowed. Otherwise the detection will be very uncertain or even impossible.

In works by Yagodin and coworkers [2-4], a liquid-liquid extraction system based on extraction of carrier amounts from dilute H_2SO_4 with trioctylamine (TOA) was reported. A good separation between Zr and Hf is achieved. Thus, this seemed like a good starting point for an extraction system to investigate the chemical properties of rutherfordium. A schematic diagram of how this extraction system is setup with SISAK is shown in Fig. 2. Results from our initial tests with carrier free amounts with such a system are shown in Fig. 3.

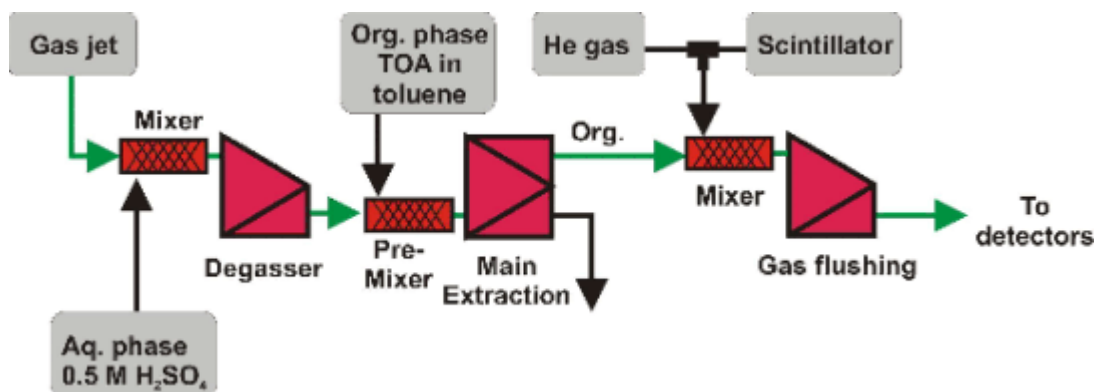


Figure 2. SISAK setup for extraction of carrier free amounts of Zr, Hf and Rf with TOA from sulphuric acid.

The data for Fig. 3 was obtained from on-line experiments at the Oslo Cyclotron Laboratory (OCL). A ~200 nA 45 MeV $^3\text{He}^{2+}$ beam was used on a combined Sr/Yb target (no isotopic enrichment for either element). The reaction products recoil out of the target and are caught on KCl-aerosol particles in a helium gas-jet. The gas-jet transports the activity in a few seconds to a chemistry lab through a 20 m capillary. Thus, we obtain 14 s $^{87\text{m}}\text{Zr}$ and 3.25 m ^{169}Hf activity for on-line SISAK experiments. The advantage of this approach, compared to using off-line produced activity dissolved directly in one of the liquid phases, is that the conditions are nearly identical to those encountered in rutherfordium experiments.

As can be seen from the right-hand panel in Fig. 3, the separation factor between the distribution ratio for Zr and Hf is on average 5.7. This is high enough to satisfy condition no. 1 in the list above. Experiments to optimize this separation with respect to reagent concentrations are under way and the results will be reported at the TAN'03 conference.

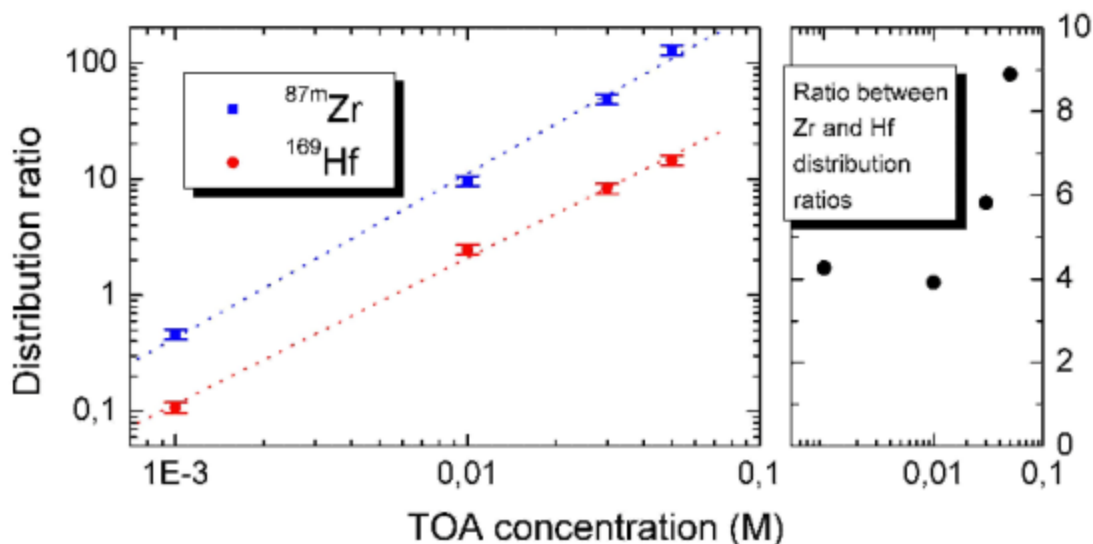


Figure 3. On-line extraction curves for Zr and Hf using 0.5 M H_2SO_4 aqueous phase and various TOA concentrations in toluene as organic phase.

In extended tests of this chemistry we found no adsorption or other unwanted effects between the chemicals used and the SISAK equipment. Thereby, condition no. 2 above is met. By comparing batch extractions performed at equilibrium conditions and on-line extraction, the difference was found to be small. This indicates that condition no. 3 is also met, a slow system would not have approached the equilibrium distribution-ratio. Finally, the quenching after contacting the organic phase with the sulphuric-acid aqueous phase was found small enough to not be of any major concern. Thus, the extraction system described here looks very promising as a system for future chemical studies of rutherfordium. More details and results will be presented at the TAN'03 conference.

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Evidence for a very noble element 112

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In recent years, chemical properties have been investigated for transactinide elements up to hassium (Hs, element 108). It could be shown, that hassium forms a very volatile tetroxide [1] and that this tetroxide adsorbs strongly on a sodium hydroxide surface [2]. Both investigations confirm for hassium a typical behavior of a group 8 element in the transition element series of the periodic table.

Due to relativistic effects in the electron shells, increasing deviations of the periodicity of chemical properties along the rows of the periodic table are expected to occur for the heaviest elements. In this context element 112 is exceptional. From the systematics of the periodic table element 112 is expected to be a member of group 12. Hence, it should behave like a volatile metal similar to mercury. However, due to its closed shell $[Rn]5f^{14}6d^{10}7s^2$ electronic structure and the mentioned relativistic effects, the relativistic stabilization of the $7s^2$ electron orbital could be so strong that element 112 might behave like a noble gas, similar to radon [3,4].

Indeed from two experiments performed at Dubna [5,6] it was concluded that element 112 does not behave like mercury. Products from the reaction $^{48}\text{Ca} + ^{238}\text{U}$ that form a long-lived spontaneously-fissioning isotope of element 112 ($^{283}112$, $T_{1/2} = 3$ min) [7-9] were continuously transported with a carrier gas to a counting device consisting of gold covered PIPS detectors followed by a gas-ionization chamber. Hg-isotopes produced in fusion reactions of ^{48}Ca with the ^{nat}Nd admixture in the target, were quantitatively adsorbed on the noble metal covered detectors, while element 112 was detected in the adjacent gas ionization chamber. Hence, this experiment yielded evidence that element 112 does not adsorb on gold at room temperature, and seems therefore to behave like a very inert metal or even like a noble gas.

In the studies of hassium tetroxide performed by our collaboration the IVO (In-situ Volatilization and On-line counting) device [10] was used. This technique permits *in-situ* thermochromatographic measurements of deposition temperatures of very volatile species on inert surfaces. Based on the expected inertness of element 112 we decided to apply a modified IVO technique for its chemical investigation. Products of the heavy ion induced nuclear fusion reaction recoiling out of the target were thermalized in dried 1 l/min helium carrier gas. The inner surface of the recoil chamber was completely covered by a quartz insert to prevent adsorption of volatile metallic reaction products. Gaseous products were swept out of the recoil chamber through an open quartz column to an oven with a quartz wool filter heated up to 850°C. Aerosol particles produced accidentally by e.g. beam particle induced sputtering processes in the beam dump were stopped in this filter. Separation factors of about 10^7 have been determined for lanthanides (model elements for heavy actinides) in test experiments with ytterbium, produced in the reaction $^{142}\text{Nd}(^{20}\text{Ne};6n)^{156}\text{Yb}$. Volatile products that passed this filter were transported through a 10 m long PFA-capillary to a Ta/Ti-getter kept at 1000°C. The getter served as trap for trace

amounts of water and oxygen. It was experimentally verified that the transport of carrier free amounts of mercury and radon occurred with almost no loss through the PFA or quartz capillary tubes at room temperature and through the Ta/Ti-getter. Finally, the gaseous products were injected into the modified detector COLD (Cryo On-Line Detector) [1]. This device consists of an array of 32 silicon PIN-photodiodes ($10 \times 9.8 \text{ mm}^2$ active area) mounted in a Teflon coated copper channel at a distance of 1.6 mm opposite to a gold covered surface, forming a rectangular gas chromatographic column. The gold surface was produced by vapor deposition of gold on a copper frame. A negative temperature gradient from $+35^\circ\text{C}$ to -187°C (see Fig. 1, black line) was established along this chromatographic channel using a thermostat heating and a liquid nitrogen cooling. The whole detector set-up was placed in a vacuum tight steel box kept at 900 mbar to isolate it thermally against ambient air.

Event-by-event spectroscopy in a 2π -detection geometry provided the identification of nuclides that were deposited on the gold surface. Calibration of the PIN-photodiodes was performed by α -decaying ^{219}Rn emanating from a ^{227}Ac source and its daughters ^{215}Po and ^{211}Bi . The determined energy resolution was 40-70 keV except for a few detectors that suffered from a reduced resolution of only 100-180 keV. This new set-up was tested on-line with short-lived Hg-isotopes produced in nuclear fusion reactions of ^{20}Ne and ytterbium (enriched in ^{168}Yb) at the PHILIPS cyclotron at the Paul Scherrer Institute and with ^{219}Rn emanating from a ^{227}Ac source. The efficiency of detecting a fission fragment was 77 %. With $^{186-190}\text{Hg}$ and ^{219}Rn an overall process efficiency of about 60 % and a transport time of less than 25 s was determined [11].

In February/March 2003 three banana shaped segments of a ^{238}U target (average thickness 1.6 mg cm^{-2}), prepared on 2.33 mg cm^{-2} thick Be foils, were mounted in the rotating target assembly ARTESIA [12] and were bombarded by $1.9 \times 10^{12} \text{ }^{48}\text{Ca}^{7+} \text{ s}^{-1}$ at a Gesellschaft für Schwerionenforschung mbH/UNILAC energy of 346 MeV. After passing the 3.7 mg cm^{-2} Be vacuum window and the target backing-foil the ^{48}Ca projectile energy was degraded to 239 MeV. The energy inside the ^{238}U target was then 222 – 239 MeV. During 16.8 days 2.8×10^{18} ^{48}Ca particles were accumulated on the target. One of the three banana shaped segments of the U_3O_8 target contained $21.7 \text{ } \mu\text{g cm}^{-2} \text{ natNd}$ in order to produce α -decaying Hg-isotopes, mainly in the reaction $^{142}\text{Nd}(^{48}\text{Ca}, 4-6n)^{184-186}\text{Hg}$. Since Rn-isotopes were produced in nuclear transfer reactions [13] it was possible to compare the chemical properties of element 112 with both mercury and radon during the entire experiment. The volatile reaction products were transported to the COLD detector with 1 l/min helium. The Hg-isotopes were completely deposited on the gold surface opposite the first nine detectors. About 65 % of ^{220}Rn were adsorbed in the low temperature part of the COLD detector (see Fig. 1).

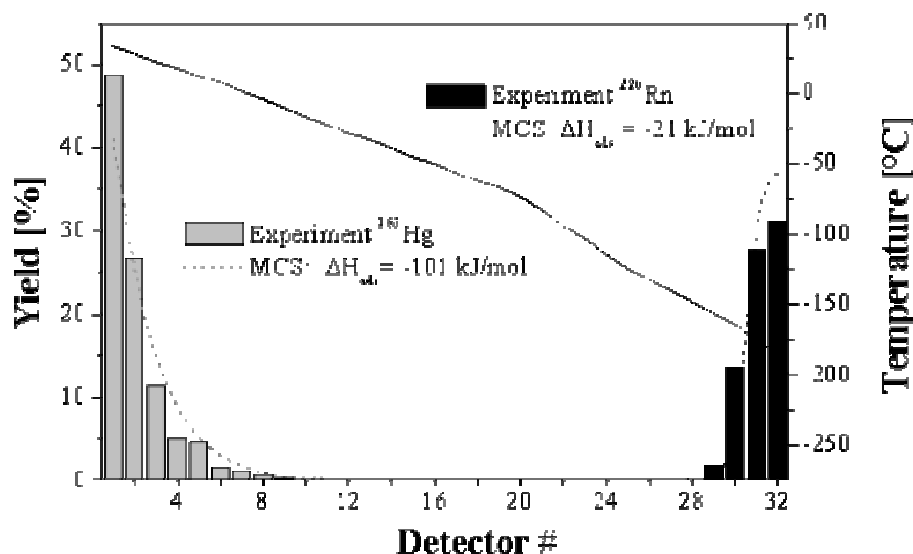


Figure 1. Thermochromatograms of ^{185}Hg (grey bars, left-hand scale) and ^{220}Rn (black bars, left-hand scale) on COLD at a helium carrier gas flow of 1 l/min. Also shown are Monte Carlo simulations of the observed depositions (grey and black dashed lines, left hand scale). The temperature gradient is indicated (black line, right-hand scale).

The spontaneous, diffusion controlled deposition of mercury on gold agrees well with literature values ($\Delta H_{\text{ads}} = -101 \pm 2$ kJ/mol) [14]. For radon the deposition distribution is reproduced assuming an adsorption enthalpy of $\Delta H_{\text{ads}} = -21 \pm 1$ kJ/mol. This value is somewhat lower compared to a literature value $\Delta H_{\text{ads}} = -29 \pm 3$ kJ/mol for radon on gold as measured under molecular flow conditions [15]. We can therefore not exclude that at these very low temperatures the gold surface is covered by a thin ice layer. Indeed, in earlier thermochromatographic experiments of radon on ice surfaces an adsorption enthalpy of $\Delta H_{\text{ads}} = -20 \pm 2$ kJ/mol was found [16]. Moreover, a careful analysis of the resolution of the α -spectra yielded evidence for an ice formation at temperatures below about -90°C (detector #21). This corresponds to a dew point of water at a partial pressure in the helium carrier gas of 0.2 ppm.

During the experiment 12 fission-like events (with energies above 40 MeV) were detected (Fig. 2). A background measurement performed after the run clearly indicated a non-zero background with scattered events along the entire array at a count-rate of approximately 0.0055 events/detector and day.

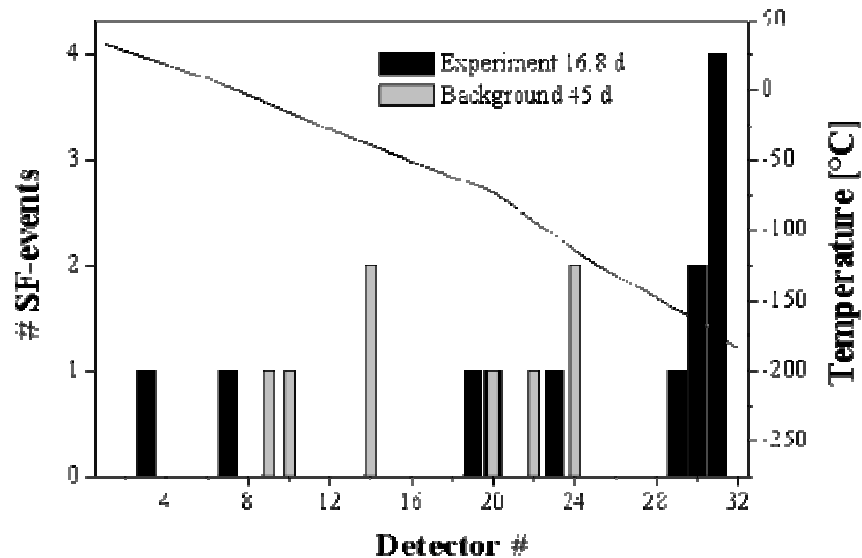


Figure 2. Observed events (with energies > 40 MeV) throughout the $^{48}\text{Ca} + ^{238}\text{U}$ experiment (black bars, left-hand scale) and during the background measurement performed immediately after the run (grey bars, left-hand scale). The temperature gradient is indicated (black line, right-hand scale).

The assignment of the measured SF events to the decay of $^{283}112$ is only convincing if no actinides are found along the detector array. Therefore, a very careful analysis of the α -spectra was performed. First, the quartz wool filter kept at 850°C was leached with concentrated nitric acid. From the solution a sample was prepared to measure off-line α - and SF-events. Pronounced peaks of $^{226-228}\text{Th}$, $^{224-226}\text{Ac}$, and $^{221-228}\text{Ra}$ were observed but no SF-decays detected during a counting time of 30 days (Fig. 3).

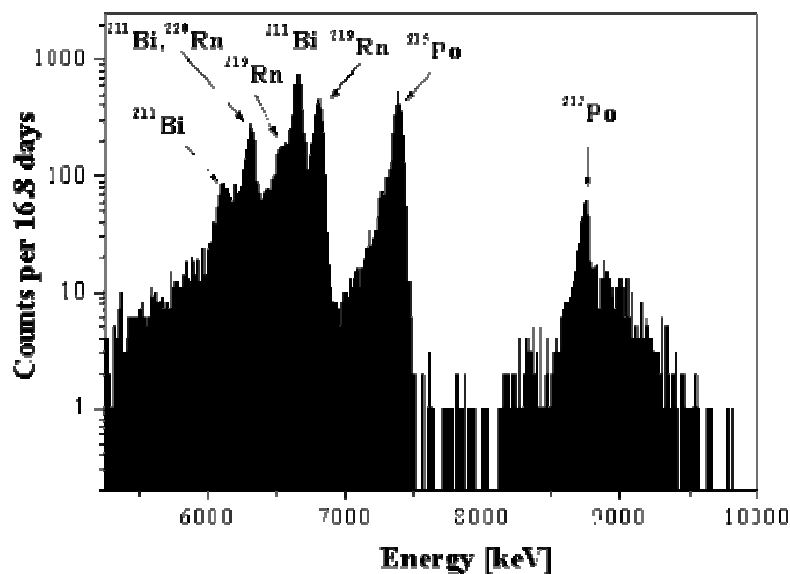


Figure 3. α -spectra of detector # 21 in the energy-range between 5.3 MeV and 10 MeV.

In addition, a thorough analysis of the recorded 32 α -spectra did not indicate any α -peak that might be assigned to a heavy actinide nuclide. Moreover, it is extremely unlikely, that any isotope of radon has a SF-branch. Hence, we assign most of the measured SF events to an isotope of element 112, presumably $^{283}112$.

In the detectors 29, 30 and 31 a total of 7 events were measured during the experiment at an expected background of 0.28 events. This deposition peak almost coincides with the deposition peak of radon. Already this preliminary data from the ongoing data analysis of the experiment allow us to conclude, that our experiment yielded strong evidence for a very noble element 112. The final results will be presented in our contribution.

Acknowledgements

We would like to thank the crews of the Gesellschaft für Schwerionenforschung mbH UNILAC and of the Paul Scherrer Institut Philips Cyclotron for providing stable and intense beams of ^{48}Ca and ^{20}Ne . We are indebted to the staff of the Laboratory for Micro- and Nanotechnology at Paul Scherrer Institute for adapting the PIN-diodes for the COLD. These studies were supported in part by the Swiss National Science Foundation.

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Investigation of alpha-electron coincidences in data from liquid scintillation detection

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Introduction

SISAK^a is a fast, chemical-separation system for liquid-liquid extraction. The system is described in another contribution to TAN'03 and in e.g. references [1, 2].

During recent years, work has been undertaken to deploy SISAK in studies of the chemical properties of the transactinide elements ($Z \geq 104$) [1, 3-6]. The only suitable detection method found was liquid-scintillation (LS) detection [7], mainly because of the rather high flow rates (0.5-2.0 mL/s) encountered in the SISAK system. Other detection methods usually require either thin, dry samples or very thin liquid films. No suitable method was found to prepare such samples without an unacceptable time delay between separation and detection.

In December 2000 the first successful transactinide experiment [3] with SISAK was performed at the Lawrence Berkeley National Laboratory (LBNL) in Berkeley, USA. This experiment proved that it was possible to extract and detect the transactinide ^{257}Rf with SISAK. ^{257}Rf has a half-life of about 4 s, and the cross section is about 12 nb [8]. The activity is delivered to the chemistry apparatus with a gas-jet transport system. With the SISAK system the gas-jet activity is continuously dissolved in an aqueous phase, then mixed with an organic phase containing a suitable extraction agent, separated and added to a liquid scintillation cocktail for α detection. The whole operation is on-line and continuous and SISAK is probably the fastest system for transactinide studies in the *liquid* phase available today. The on-line LS detection system used for SISAK experiments was developed in Mainz by Wierczinski [7] and co-workers and has continuously been improved [1,3,9]. The search for improvements continue and as a part of this a study of conversion electrons in coincidence with α particles was initiated and is reported here.

The effect of conversion electrons on α -liquid scintillation spectra

If an α decay is populating an excited level in the daughter nucleus and this level deexcites by emission of a conversion electron, the resulting α spectrum can become seriously distorted. This is because the light emitted from the scintillator due to an electron is about 8-12 times as high as from an α particle (due to the differences in the LET (Linear Energy Transfer) between the respective particles and the medium they interact with) [10]. Thus, a 50 keV electron will cause emission of light pulses equivalent to about 0.5 MeV of α energy. The result is that α spectra obtained from sources with coincident or near coincident conversion electrons will have distorted α peaks.

In measurement of transactinides the production rate is rarely high enough to obtain α spectra with prominent α peaks. Instead one usually relies on observing correlated chains of α particles with the correct energy and time sequence. However, when LS detection is used, α - electron coincidences might change the observed α energy so much that it falls outside the energy window. This together with the fact that many transitions in the transactinides are highly converted, can lead to a serious loss of observed events. E.g. in the ^{257}Rf SISAK experiments the correlated daughter to ^{257}Rf is ^{253}No . The decay of ^{253}No feeds a level at 300 keV in ^{249}Fm . From systematics one expects a conversion coefficient of about 0.05,

which means that about 1 out of 20 ^{253}No α decays will be correlated with an electron of around 150 keV (the K electrons are bound by 150 keV for Fm atoms), see Fig. 1. Thus, about 5% of the α particles from ^{253}No will be observed with more than 1 MeV of extra energy, which is outside the energy window used.

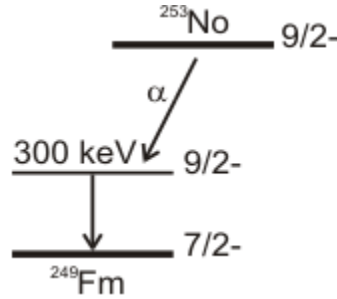


Figure 1. Simplified decay scheme of ^{253}No , showing the converted transition in ^{249}Fm ($\alpha_{\text{Total}}=0.05$).

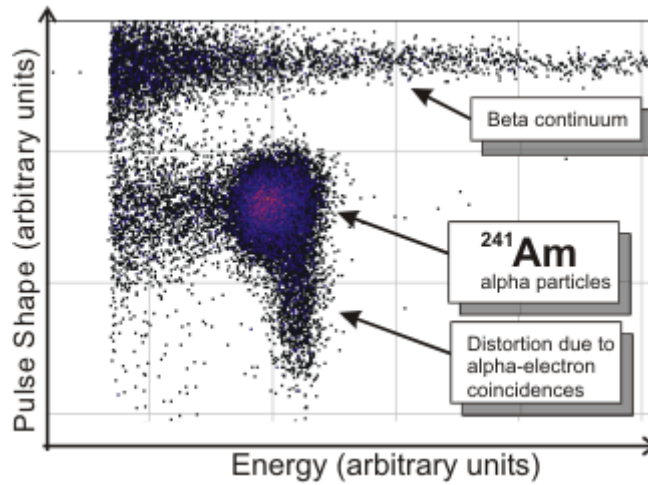


Figure 2. Measured pulse shape vs. energy plot of ^{241}Am α particles.
The half life for the intermediate level in ^{241}Np is 67 ns.

The aim of this work is to find a method to spot such α -electron coincidences and correct the observed energy to coincide with the energy observed for a pure α . Since the SISAK system already employs pulse-shape analysis to discriminate between α 's and β 's [10], it was natural to investigate if α -electron coincidences would change the pulse shape signal (basically a measurement of the length of the falling edge of the light pulses from the scintillator). As can be seen from Fig. 2, this seems to be the case: Energy vs. pulse shape is plotted in a contour plot for data obtained from ^{241}Am . The long tail of the α peak can be attributed to α -electron coincidences. The shape of the tail can be understood by taking into account the half life of the intermediate level. For ^{241}Am this half life is equal to 67 ns [11], as shown in Fig. 3. For another americium isotope with a similar type of decay, but with a shorter half life of only 1.4 ns [12] (Fig. 3) we can see that the pulse shape is much less effected, see Fig. 4.

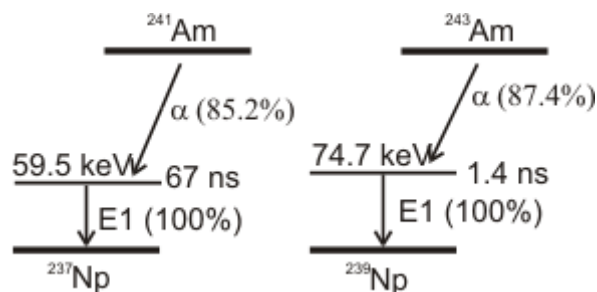


Figure 3. Simplified decay scheme of ^{241}Am and ^{243}Am .

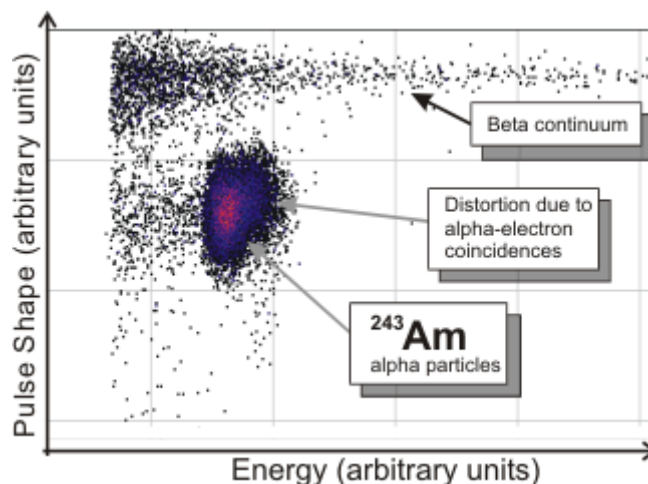


Figure 4. Measured pulse shape vs. energy plot of ^{243}Am α particles.
The half life for the intermediate level in ^{239}Np is 1.4 ns.

Digital Acquisition

From this data it can clearly be seen that the α -electron coincidences will change the LS data, both with respect to energy and pulse shape. It is also clear that the analog electronics used to obtain the data in Fig. 2 and 4 is not precise enough to distinguish between pure α events and α -electron coincidences. Therefore, experiments are under way in which a digital-acquisition system is used to sample each pulse from the scintillator and not only measure its width as the analog electronics do. With the pulses available a much more sophisticated analysis of the pulse shape can be performed, and hopefully this will enable both a better determination of the type of signal (β , α , or α -electron), but also correction for the additional energy added by the extra excitation of the scintillator caused by the electron.

Work with the digital acquisition system is under way and results will be presented at the TAN'03 conference.

Acknowledgements

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Suitability of extraction systems with macrocyclic ligands for the study of rutherfordium

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Introduction

For the first time, the fast, automated liquid-liquid extraction system SISAK was recently successfully used to study the chemical behavior of element 104, rutherfordium [1]. This was made possible by coupling the SISAK system to the Berkeley Gas-filled Separator (BGS). The BGS was used to achieve a physical pre-separation of the desired species from the beam and unwanted reaction products. This pre-separation reduced the background due to the scattered beam and other reaction products substantially and allowed for the detection of rutherfordium atoms without any interference of undesirable activity. The lack of interfering reaction products has several advantages for the design of chemistry experiments with transactinides. In addition to simplifying the detection and data analysis it allows the use of a different class of extraction systems in future SISAK and other chemistry experiments.

The first goal of experiments to study the chemical behavior of transactinide elements is to establish the position of these elements in the periodic table. Then, the properties of the transactinides are systematically compared with those of their lighter homologues and pseudo-homologues to gain further insight into the periodicities within a group of the periodic table and evidence for the influence of relativistic effects. Differences in extraction behavior can be used to differentiate between the individual elements of a group.

In the past, it was necessary to select extraction systems that removed all interfering reaction products and left only the element of interest. Consequently, a very high decontamination factor between the element of interest and interfering activity had to be favored over a high selectivity between the different homologues within the group being studied.

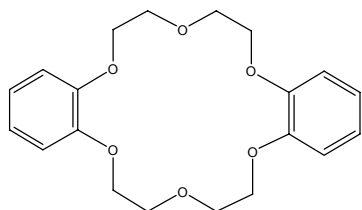
Due to the success of the experiments with pre-separated activity, selectivity between the members of the same group of the periodic table can now be favored over efficient separation from elements belonging to other groups when designing extraction systems for future experiments [2]. This affects the usefulness of extraction systems for the study of transactinide elements and changes their selection criteria. In addition it also gives access to other classes of extraction systems that previously have not been considered when developing solution chemistry experiments.

These additional extraction systems need to be studied regarding their suitability for future experiments with transactinide elements. After the success of the first experiments with pre-separated rutherfordium isotopes, it was decided to start searching for different extraction systems that could be used to study the chemistry of element 104. The extraction systems need not only to be evaluated for their usefulness for future SISAK experiments, but for other automated systems and manual extraction experiments as well.

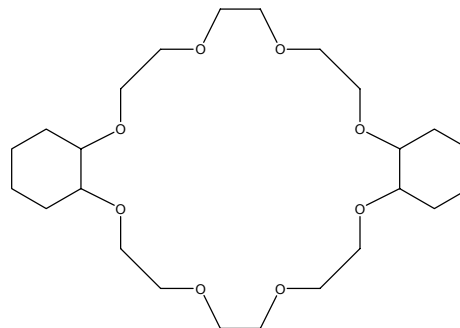
Macrocyclic ligands and their application

Several highly selective extractants are currently under investigation in our group, especially systems with macrocyclic ligands.

A macrocyclic ligand can be defined as a compound comprising a ring of at least nine atoms including at least three donor atoms oriented so as to bind to a metal atom. These ligands are a special type of polydentate ligands in which the ligating atoms are constrained in a large ring encircling the metal ion. Examples for such ligands are polyethers in which the ether oxygen atom, separated by two methylene groups each, lie in a nearly planar arrangement about the central metal atom and the remainder of the molecule lies in a “crown” arrangement. All of the oxygen atoms “point” inward toward the metal atom, and these macrocycles form stable complexes with alkali- and other metals [3]. Examples of crown ethers that show promise for experiments with group 4 elements, dibenzo-18-crown-6 (1) and dicyclohexano-24-crown-8 (2), are shown below. Other examples of such macrocyclic ligands include thiacrowns and calixarenes.



1



2

The high stability of the complexes of certain metals with macrocyclic ligands and accordingly the high selectivity of such ligands is generally attributed to a size effect. It depends on how closely the metal ion fits into the gap in the center of the ligand. But the differences in metal ion affinities in the gas phase compared to in solution suggest that solvent effects play an important role as well.

The high selectivity of extraction systems with macrocyclic ligands is used in a multitude of applications in analytical and technical chemistry. The coordination chemistry of macrocyclic ligands and alkali and earth alkali metals has been studied in depth [4], and these ligands are most commonly applied for the separation of these metal ions. In addition, these extractants show also promise for the separation of other transition and main group metals [5].

Reaction kinetics is another factor in evaluating the suitability of an extraction system for chemistry with transactinide elements. This factor may even be more important than a high selectivity between the members of a group of the periodic table.

Unfortunately, the size of the organic molecules used as extractants can have a large effect on the kinetics of the reactions. While the time necessary to complete a reaction can be a secondary concern for many applications, it is of great importance for the study of the transactinide elements. Due to the short half-life of the elements studied it is necessary to choose chemical systems that reach equilibrium as fast as possible. This severely restricts the choice of extraction systems with macrocyclic ligands that can be used for the study of rutherfordium or other transactinide elements. The kinetics of any extraction system that shows promise needs to be studied very thoroughly.

The use of different crown ethers, e.g., dicyclohexano-18-crown-6 and dibenzo-18-crown-6, for the separation of zirconium and hafnium has been reported previously in the literature [6,7]. None of these studies were conducted under conditions that can be applied to the study of rutherfordium.

The usefulness of these extractants in experiments with substantially shorter contact and reaction times needs to be studied. In addition the suitability of other systems needs to be also tested.

Experimental

In this work the extraction of the lighter homologues and pseudo-homologues of rutherfordium with different macrocyclic ligands from mineral acid solutions was studied using tracer activities with short and medium half-lives.

Offline experiments were performed using ^{88}Zr ($T_{1/2}=83.4$ d) and ^{175}Hf ($T_{1/2}=70.0$ d) as tracer activities. In addition, on-line experiments were performed at the 88-inch cyclotron at LBNL. Short-lived isotopes of Zr and Hf were produced by bombarding a $^{\text{nat}}\text{Gd}$ and a ^{124}Sn target with an $^{18}\text{O}^{4+}$ and a $^{50}\text{Ti}^{11+}$ beam, respectively. The zirconium and hafnium isotopes produced were separated from the beam and interfering reaction products using the BGS. After traveling through the BGS, the products passed through a thin Mylar window into the Recoil Transfer Chamber (RTC) [8]. Inside the RTC, the recoils were stopped in helium and transported to the chemistry setup using a potassium chloride aerosol gas jet.

The aerosols containing the activity were deposited on platinum foils and dissolved in mineral acid of appropriate concentration to conduct the extraction experiments.

The extraction of zirconium and hafnium with different macrocyclic ligands was studied from dilute and concentrated mineral acids, mainly hydrochloric acid. The distribution ratios for the elements were determined as a function of acid and ligand concentration.

The extraction experiments were performed on a time scale relevant for experiments with transactinide elements (< 2 minutes). The kinetics of the reaction was studied by varying the contact time during mixing and the time allowed for phase separation. In addition, the influence of different solvents on the extraction was studied.

The results of these experiments will be presented.

Acknowledgement

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Development of a selective separation method for element 107 – bohrium – based on fast liquid-liquid extractions

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Abstract

Liquid-liquid extraction has been used to develop a fast separation procedure of the homologues of element 107 (bohrium, Bh) from other reaction products, which can simultaneously be produced in the heavy ion reactions used for transactinide production. Alpha-hydroxyisobutyric acid has been used as complexing agent in the aqueous phase solution. The organic phase solution consisted of trioctylamine in Shellsol T. A quantitative extraction of technetium and rhenium has been observed in the pH range from 1.5 to 5.5, with a good separation from most other studied elements, except for iodine, which has been extracted up to 50 % and niobium, which only can be separated from the group VII elements at high pH-values.

Introduction

Knowledge about the chemical properties of transactinide elements allows to determine their position within the periodic table of the elements. If they behave similar to their lighter homologues they can simply be placed under the corresponding group. If their chemical behavior is influenced by relativistic effects, positioning within the table of elements may be more difficult.

Transactinide elements are studied using different chemical separation methods including column separation, gas chromatography and liquid-liquid extraction. Usually only a few atoms of these elements are produced during an accelerator experiment and the half-lives of these elements are in the range of seconds to minutes. Therefore the separation method used has to be very fast, highly selective for the element of interest, very efficient and also the detection method should be capable to measure single atoms with high accuracy and efficiency.

The SISAK (Short-lived Isotopes studied by the AKUFVE technique) [1] uses fast rotating centrifuges to perform continuous liquid-liquid extractions. In the past, this system has been coupled with an on-line alpha-liquid scintillation system to be able to continuously measure alpha-decaying transactinides.

Presently new developments are taking place to further improve the performance of the SISAK system: to overcome problems with high overall activity and resulting detection difficulties a pre-separation of the produced transactinide with a gas-filled separator is investigated. First experiments have shown promising results [2]. Secondly, the design of a so-called 'micro-SISAK' system is going on, which should reduce the total amount of aqueous and organic solutions used for the separation [3] and also will allow operation of the system at lower flow-rates. In this case, detection of the extracted nuclides using semi-conductor detectors is also investigated.

However, liquid-liquid extraction still remains the main principle on which the separation is based. Such a liquid-liquid extraction procedure is usually investigated by performing experiments with the lighter homologues of the transactinide of interest as well as some neighbouring elements. In the case of bohrium (element 107), technetium and rhenium are used as homologues and are separated from group 4, 5 and 6 elements, as well as some di- and tri-valent metals and one actinide element.

Experimental

Radionuclides

Table 1 shows the radionuclides used for developing the extraction procedure. If they were not commercially available, production procedures were developed to obtain non-carrier-added radionuclides. These production procedures were usually based on neutron irradiation of certain compounds at the HOR research reactor of the Interfaculty Reactor Institute in Delft, The Netherlands. Ideally, (n,p)- and (n,α)- reactions were used to produce the short-lived nuclides. Examples are the production of non-carrier-added ^{64}Cu and ^{58}Co . Other nuclides were produced by beta-decay of the corresponding mother nuclide: ^{95}Nb and ^{105}Rh were produced in this way. Before the radionuclides were used for the extraction experiments, they were chemically separated from their original matrix or mother nuclides.

Table 1. Radionuclides used to develop an extraction procedure for bohrium and their half-lives.

Radionuclide	$t_{1/2}$
$^{99\text{m}}\text{Tc}$	6.02 h
^{186}Re	3.78 d
^{188}Re	16.98 h
^{95}Nb	31.15 d
^{105}Rh	1.47 d
^{103}Ru	39.35 d
^{239}Np	2.36 d
^{131}I	8.04 d
^{65}Zn	244 d
^{64}Cu	12.71 h
^{58}Co	70.78 d

Extractions

The aqueous solution consisted of 1 M α-hydroxyisobutyric acid, 0.01 M potassium bromate to ensure the +VII oxidation state of the elements, and 0.22 M dodecanol to improve the phase separation. The pH-value was varied using either hydrochloric acid or ammonia. The organic solution consisted of 2 % vol trioctylamine (TOA) in Shellsol T. Liquid-liquid extractions were performed in polyethylene tubes: the tubes were sealed at one end and 0.5 ml of the two phases including the nuclide of interest were added in the tube. After sealing the other end of the tube it was shaken 1 minute using a Vortex apparatus. The phases were separated by centrifugation and an aliquot was removed from both phases

and measured using Ge(Li) semiconductor detector. Extractions were carried out three times and the average value is given for the extraction yield.

Results and Discussion

Figure 1 shows the results obtained for extraction of the above mentioned nuclides: Tc and Re are extracted quantitatively into the organic phase throughout the whole pH range from 1.6 to 5.0. Niobium as a homologue of element 105 is extracted in high yields at lower pH values, but the yield decreases for higher pH values until it is extracted less than 5 % at pH values around 5. This result is in agreement with earlier experiments [4]. Iodine is extracted with a yield of about 50 % throughout the whole pH range. Cobalt, copper, neptunium and zinc are not extracted at all. The extraction yields of rhodium and ruthenium increase slightly at higher pH values and reach a maximum yield of about 17 % and 30 % and pH values 5.5 and 4.5, respectively.

First results obtained with molybdenum show negligible extraction yields and are not yet included into figure 1.

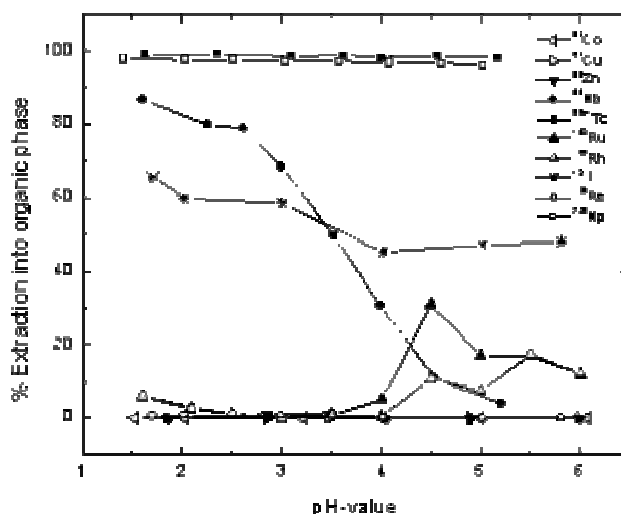


Figure 1. Extraction yields for different nuclides. Organic phase: 2 % Vol trioctylamine in Shellsol, aqueous phase: 1 M alpha-hydroxyisobutyric acid, 0.01 M potassium bromate, 0.22 M dodecanol.

The results suggest that this extraction system using alpha-hydroxyisobutyric acid may be used at pH values above 5 for a quantitative separation of element 107 and its homologues from other reaction products.

Future work

Not only molybdenum but also tungsten isotopes will be used in future experiments to ensure the selective separation of group 6 from group 7 elements. Addition of a small amount of H₂O₂ to the aqueous phase should result in a decreased extraction yield of niobium and will also be investigated. Furthermore, on-line experiments with even shorter lived isotopes are necessary to ensure that the extraction kinetics is indeed fast enough for future continuous separations using the SISAK system.

Also, if on-line alpha-liquid-scintillation counting will be used as detection method for the transactinide element, the organic phase should consist of an aromatic solvent, such as toluene. Although earlier experiments suggest that the above mentioned extractions are in general possible with aromatic solvents [5], some experiments have to be carried out to ensure identical extraction yields as when using Shellsol.

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The new isotopes of element 107: Bh-266 and Bh-267 and the chemistry of bohrium

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The early history of bohrium

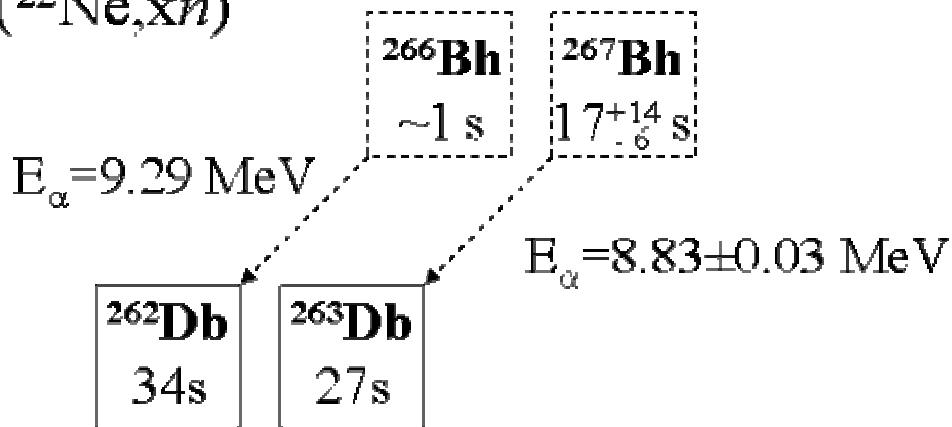
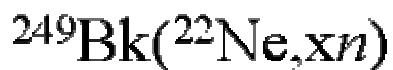
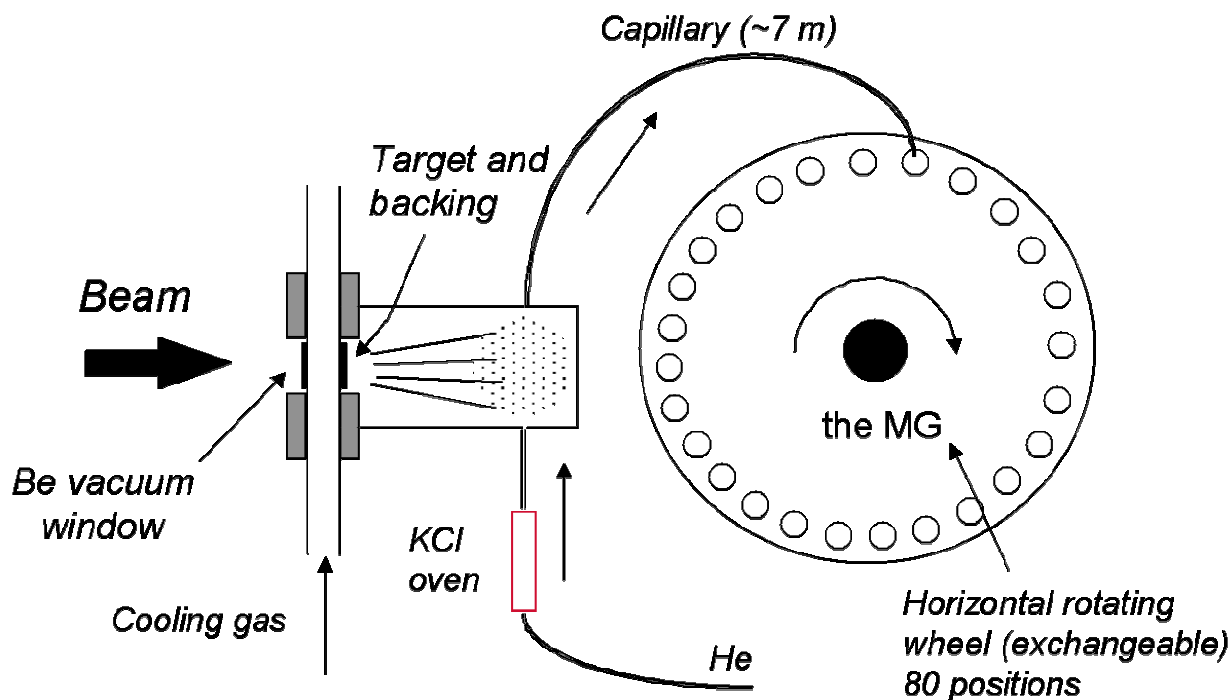
Bohrium was first identified in 1981 by Münzenberg *et al.* as the isotope $^{262}\text{Bh}^m$ produced in the $^{209}\text{Bi}(^{54}\text{Cr},n)$ reaction [1] using the velocity filter “Separator for Heavy Ion Production” (SHIP) at the Gesellschaft für Schwerionenforschung (GSI), Darmstadt, Germany. Earlier performed experiments initially claimed synthesis of element 107 via the $^{54}\text{Cr}(^{209}\text{Bi},2n)$ reaction, based on observation of the spontaneous fission activity from the decay of ^{261}Bh . However, in subsequent experiments spontaneous fission activity was not detected, and ^{261}Bh was unambiguously identified by correlation with its α -decay daughter ^{259}Ha . [2]. To date, no spontaneous fission activity has been observed that can be attributed to spontaneous fission of any bohrium isotopes and a low upper limit on the spontaneous fission branch was set. The properties of the isotopes of bohrium known previous to this work are: ^{261}Bh ($T_{1/2}=11.8$ ms; $E_{\alpha}=10.40, 10.10, 10.03$ MeV [2]), ^{262}Bh ($T_{1/2}=102$ ms; $E_{\alpha}=10.06, 9.91, 9.74$ MeV [2]), $^{262}\text{Bh}^m$ ($T_{1/2}=8$ ms; $E_{\alpha}=10.37, 10.24$ [2]), and ^{264}Bh ($T_{1/2}=440$ ms; $E_{\alpha}=9.62, 9.48$ MeV [3]).

The isotopes 266 and 267

Experiments were undertaken to try to produce and identify the new neutron-rich isotopes of bohrium, ^{266}Bh and ^{267}Bh . These isotopes were predicted to have significantly longer half-lives than previously known bohrium isotopes, possibly long enough to enable the first studies of bohrium chemical properties in subsequent experiments. Previous attempts to identify these isotopes by chromatographic separation have failed [4, 5]. Based on predicted Q -values for electron capture and α -decay, ^{266}Bh and ^{267}Bh should decay predominantly by α -emission and possibly by spontaneous fission (SF). The α -particle energies and half-lives for these isotopes are expected to be in the range of 8.7–9.3 MeV [6] and 1-20 seconds [7]. The previously reported decay characteristics of their Ha and Lr daughter nuclei, are: ^{262}Ha ($T_{1/2}=34$ s; $E_{\alpha}=8.45, 8.53, 8.67$ MeV [8]), ^{263}Ha ($T_{1/2}=27$ s; $E_{\alpha}=8.35$ MeV [9]), ^{258}Lr ($T_{1/2}=3.9$ s [10]; $E_{\alpha}=8.60, 8.62, 8.57, 8.65$ MeV [8]), and ^{259}Lr ($T_{1/2}=6.34$ s; $E_{\alpha}=8.45$ MeV [10]). Kratz *et al.* [9] report an α -particle energy of 8.35 MeV for ^{263}Ha , but other measurements [11] indicate that ^{263}Ha might also decay by emission of 8.41-MeV α -particles.

Using these predictions as a guide, ^{267}Bh and ^{266}Bh were produced in bombardments of a ^{249}Bk target with 117-MeV and 123-MeV ^{22}Ne ions. Identification was made by observation of correlated α -particle

decays between the bohrium isotopes and their daughters by using our rotating wheel (MG) system. A parent-daughter stepping mode was used to provide detection of α - α correlations with a greatly reduced background [12]. After the end of bombardment and careful analysis of the data, it was found that four atoms of ^{267}Bh were produced during the experiment. ^{267}Bh was produced with a cross-section of ~ 70 pb and was found to decay with a $17 (+14/-6)$ s half-life by emission of α particles with an average energy of 8.83 ± 0.03 MeV. One atom of ^{266}Bh was observed, decaying within one second by emission of a 9.29-MeV α particle [13].



The chemistry of bohrium

The arrangement of the chemical elements in the periodic table indicates similarities of chemical properties, which reflect the elements' electronic structure. For the heaviest elements, however,

deviations in the periodicity of chemical properties are expected due to relativistic effects. Bohrium is expected to be a group seven element and should form oxychloride species in the gas phase in an analogous fashion to rhenium and technetium. During test experiments with rhenium and technetium [14, 15] only one chemical species, assumed to be $[\text{Re/Tc}]\text{O}_3\text{Cl}$, was seen with the thermochromatography apparatus.

Pershina *et al.* predict that the electronic structure of BhO_3Cl should be very similar to TcO_3Cl and ReO_3Cl . The calculated energy gap (ΔE) and ionization potential (IP) increase from Tc to Bh for the MO_3Cl species. The 7+ oxidation state should also increase in stability down the group following the increasing ΔE . The Bh species is also more covalent than the other two species which they attribute to relativistic effects seen in the component atomic orbital [16, 17]. These effects also influence dipole moments and dipole polarizabilities, which should dominate intermolecular or molecule-surface interactions. These interactions are the basis for volatility that they expect should decrease down the group, i.e. that BhO_3Cl should be less volatile than ReO_3Cl which should be less volatile than TcO_3Cl .

Using the same reaction as for the previous experiment, a volatility experiment to study bohrium chemistry was performed at the Paul Scherrer Institute (PSI), Switzerland. The behavior of Bh was investigated at 180, 150, and 75°C. Two α -SF chains, two α - α chains, and one α - α - α decay chain, all attributed to the decay of ^{267}Bh , were observed at 180°C. At 150°C two α -SF chains were observed, and at 75°C no events were observed. Random correlations should not significantly contribute to the number of α -SF or α - α - α chains seen, but approximately one of the α - α correlations seen are expected to be due to random correlations. The unambiguous identification of Bh after chemical separation allows us to conclude that like its lighter homologues, Bh forms a volatile oxychloride compound, presumably BhO_3Cl , and behaves like a typical group seven element [18]. We found that this compound is less volatile than the oxychlorides of the lighter elements of group VII, thus confirming predictions based on its periodic position.

Assuming the Bh compound to be BhO_3Cl and applying a microscopic model of the adsorption-desorption process [19] and using the Monte Carlo code developed by Türlér to fit the measured volatility curves, the evaluated standard adsorption enthalpy (ΔH_{ads}) of BhO_3Cl on the quartz surface was determined to be $-75(+9/-6)$ kJ/mol. The adsorption enthalpies for TcO_3Cl and ReO_3Cl are -51 ± 3 and -61 ± 3 kJ/mol respectively [15]. After the quartz column, BhO_3Cl was transported to ROMA on CsCl aerosols. Unlike ReO_3Cl , TcO_3Cl is so volatile that it can not be transported with CsCl, which again indicates Bh is more like Re than Tc.

Conclusion

Bohrium has been placed decisively on the periodic table and periodic extrapolations confirmed. This first chemistry experiment with bohrium would have been impossible without an adequate candidate isotope of bohrium. These experiments were also reliant on the theoretical predictions of the chemical properties of bohrium and the theoretical predictions of the production and decay properties of the anticipated heavier isotopes of bohrium. These experimental data that we have generated, can now be re-applied to the theory to further fine-tune and increase our understanding of the fundamental processes at work [20,21]. In addition, the target material was provided by Office of Science, Office of Basic Energy Research, Division of Chemical Sciences, of the U.S. Department of Energy, through the transplutonium element production program at the Oak Ridge National Laboratory. The culmination of this collaboration, by the successful determination of the chemistry of bohrium, was only possible by the joint efforts of all the members from many different organizations.

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